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EXAFS Analysis of Co-Containing Polymers

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Abstract. In this work we present a detailed analysis of the extended x-ray absorption fine structure (EXAFS) spectra at the cobalt K-edge in a series of Co-containing polymers prepared by reaction of the Schiff-base polymer \((\text{C}_1\text{H}_7\text{N}_3)\) and a Co\(\text{X}_2\) salt, where \(\text{X} = \text{NO}_3, \text{ClO}_4, \text{Cl}\) and \((\text{SO}_4)_{1/2}\). The analysis of EXAFS data has confirmed the formation of polymeric-coordination complexes as materials with a very low crystallinity.

1. INTRODUCTION

The search for molecular ferromagnetic materials has attracted a great deal of attention in the last years because their potential technological applications. After the publication of the first works reporting the existence of organometallic compounds exhibiting ferromagnetic behavior, the possibility of preparing entirely organic-based ferromagnets has become a major challenge. Metallopolymers or coordination polymers have been sought out together with radical organic polymers as a type of magnetic polymers [1]. Metal incorporation to the polymers modifies the electrical, thermal and magnetic properties of this kind of materials, as it is the case of coordination polymers prepared from an organic polymer containing a recurring chelate group and treated with suitable metal salts to form the metal derivative[2]. The origin of their magnetic behavior may directly result from the the metal ion spins arranged as to be strongly coupled along the organic polymer backbone. However, some of these compounds have been reported to exhibit anomalous magnetic behavior and their chemical and magnetic characterization is a matter of controversy. This is the case of polymeric materials based on the tridentate Schiff-base polymer \((\text{P})\) formed from pyridine-2, 6-dialdehyde and hexamethylenediamine, and iron salts [3-5]. From the synthetic conditions one should expect a polymeric complex consisting of tridentate Schiff bases and hexacoordinated Fe(II) ions. As it is typical in related coordination compounds the iron would exhibit a low-spin \(S=0\) configuration [6] and the material would be diamagnetic. However, the magnetic studies suggest the existence of net magnetic moments in the material, that can be originated by the modification of the ligand field through the deformation of the octahedral environment of Fe, or due to small particles of magnetic Fe(III) oxides built-in within polymer. Moreover, in the case of samples prepared with the organic polymer \((\text{P})\) and a suitable solution of Co(II) salt, also anomalous behavior has been reported [7] being the origin of their magnetic behavior not clear yet. Structural characterization is, therefore, a strong requirement to understand the origin of the magnetic properties of these materials, in particular to discern between the extrinsic or intrinsic nature of the observed anomalous magnetic behavior.

In this work we present the structural characterization of the local environment around cobalt in a series of Co-containing polymers prepared by reaction of the Schiff-base polymer \((\text{C}_1\text{H}_7\text{N}_3)\) and a Co\(\text{X}_2\) salt, where \(\text{X} = \text{NO}_3, \text{ClO}_4, \text{Cl}\) and \((\text{SO}_4)_{1/2}\). The Extended X-ray Absorption Fine Structure (EXAFS) region of the absorption spectra has been analyzed by means of ab-initio multiple-scattering calculations. Polymer coordination Schiff-base Co-containing complexes were prepared following synthetic methods described in the literature [7].

2. RESULTS AND DISCUSSION

In all the studied cases, the EXAFS signals indicate the low crystallinity of the systems. Indeed, the Fourier transforms do not exhibit contributions for interatomic distances larger than 4 Å. Moreover, the modulation of the EXAFS signals is very similar for the five polymer compounds and also resembles that of the monomer reference Co(MI), although the intensity of the EXAFS structures is substantially reduced in the polymers compounds. These results indicate both, the lower crystallinity of the polymers as compared with the monomer unit, and that the atomic environment of Co in the polymers is very close to that of the monomer reference. Hence, Co atoms should be surrounded by 6 nitrogen atoms arranged in octahedral geometry and by the C atoms of the tridentate quelaate units.

To verify the reliability of this preliminary fingerprint analysis, and to determine how this environment is modified by the different Co\(\text{X}_2\) salts used in the synthesis procedure, we have performed a more detailed EXAFS analysis by using ab initio theoretical calculations at the Co K-edge by applying the code EXCURV88, described elsewhere. The computation reproduces well the experimental spectra, indicating the reliability of the structural assumptions made. In all the polymer compounds investigated there is no trace of Co-Co coordination and the local environment around Co is formed by six N atoms arranged in an octahedral layout as in the case of the monomer reference Co(MI). Moreover, nearest-neighbors present different distortions as a function of the nature of the counter-ion, X, of the different Co\(\text{X}_2\) salts used in the synthesis.

Special attention has been paid to the analysis of the Co(P)Cl-E polymer compound. For this system two different Co structural environments have been proposed: i) as in the former polymers Co should be surrounded by N atoms in the first coordination shell; ii) the Cl atoms of the salt becomes coordinated to cobalt [3,7]. We have tested these two possibilities as shown in Fig. 1. The best-fits are found when two Cl and 3 nitrogen atoms are coordinated to the central Co. On the contrary, the simulation performed by only including N atoms in the first-ordination sphere is rather unsatisfactory, showing strong differences, both in phase and intensity, between the experimental EXAFS signal and the theoretical one.
The substances synthesized in aqueous medium, which are known as Co(P)SO4, Co(P)NO3, Co(P)ClO4 and Co(P)Cl, have been revealed as amorphous coordination polymers of ionic nature in which the cobalt ion is coordinated by 6 nitrogen atoms in an octahedral arrangement. The results for the two polymers obtained through synthetic modifications, Co(P)SO4-C and Co(P)Cl-E, are different each other. In the former similar octahedral environment around Co is found, whereas for Co(P)Cl-E the Cl atoms of the salt becomes coordinated to Co.

In an octahedral crystal field, Co2+ presents a high-spin configuration (S = 3/2) and the magnetic moment expected is 5.2 μB at room temperature, due to the important orbital contribution of the 4T1g ground state. Therefore, if cooperative interactions do not exist among magnetic cobalt ions these polymeric compounds should exhibit paramagnetic behavior throughout the temperature range, in contrast to the experimental observed behavior [5,7]. Two intrinsic mechanisms can be proposed to account for such anomalous magnetic behavior. The first one lies on the possibility to find a magnetic Co-Co interaction in the polymers. However, EXAFS analysis does not reveal any trace of Co-Co coordination within the local environment around Co (8 Å). Secondly, the combined effect of crystalline distortions and spin-orbit coupling of the 4T1g level can led to a low-spin (S=1/2) ground state close in energy to the first excited level, so that deviations from the normal paramagnetic behavior can be expected at high temperature [8-10], thus explaining the anomalous magnetic behavior found. However, the same anomalous behavior is found in all these compounds despite EXAFS data address a different local structure around cobalt (from octahedral to penta-coordinated) induced upon modification of the solvent (Co(P)SO4-C vs Co(P)Cl-E). Therefore, according to the present data both possibilities can be disregarded, in good agreement to recent results [7] addressing that the anomalous behavior observed is not intrinsic to the polymeric material but due to magnetic small particles.

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References