Synthesis and characterization of cobalt(II) and zinc(II) complexes of poly(3-nitrobenzylidene-1-naphthylamine-co-succinic anhydride)

Chellaian Justin Dhanaraj, Madhavan Sivasankaran Nair *

Department of Chemistry, Manonmaniam Sundaranar University, Tirunelveli 627 012, Tamil Nadu, India

Received 17 June 2011; accepted 5 October 2011
Available online 12 October 2011

Abstract The cobalt(II) and zinc(II) complexes of poly(3-nitrobenzylidene-1-naphthylamine-co-succinic anhydride) were synthesized by the reaction of THF solution of the alternating copolymer with aqueous solution of cobalt(II) and zinc(II) acetates. The metal complexes were characterized by elemental analysis, magnetic measurements, IR, UV–Vis. and $^1$H NMR spectral studies. The elemental analysis of the metal polymer complexes suggests that the metal to ligand ratio is 1:2. Conductance measurements indicate the non electrolytic nature of both the complexes. Electronic spectrum and magnetic moment studies are taken into account for the geometry of cobalt complex. Thermal analysis data of the two metal–polymer complexes were reported. XRD data revealed the nanocrystalline nature of both the complexes. The SEM studies give the surface morphology of the complexes.

© 2011 Production and hosting by Elsevier B.V. on behalf of King Saud University.

1. Introduction

Coordination polymers are one of the most interesting topics in current chemistry and crystal engineering. The synthesis and characterization of coordination polymers have attracted much attention due to their high stability and intricate inter-

* Corresponding author. Tel.: +91 9443540046; fax: +91 462 23334363.
E-mail addresses: justindhanraj@yahoo.co.in (C.J. Dhanaraj), msnairchem@rediffmail.com (M.S. Nair). Peer review under responsibility of King Saud University.

weaving of multiple networks (Fua et al., 2006). The characterization of ion containing polymers has been the subject of numerous investigations. It has been demonstrated that the thermophysical properties of polymeric ligands can be modified by coordination to transition metal complexes (Jiang et al., 1993; McCurdie and Belfiore, 1999). The activity of metal complexes on polymer supports has normally been found to be more in comparison to metal complexes on inorganic supports (Monica et al., 2003; Liu et al., 2004; Rodrigues et al., 2004; Casagrande et al., 2004). Polymer-supported Schiff base complexes of metal ions show high catalytic activity in comparison to their unsupported analogues. The manganese(III) Schiff base complexes exhibited high catalytic activity in the oxidation of alkenes and alkanes both in homogeneous and heterogeneous conditions. The Schiff base complexes of iron(III), cobalt(II), nickel(II), copper(II) and
Zinc(II) ions have been used as catalysts in the epoxidation of cyclohexene and oxidation of phenol. Polymer-supported iron(III) Schiff base complexes have demonstrated higher activity than unsupported and polymer-supported Schiff base complexes of other metal ions. The thermal and moisture stabilities of polymer-supported Schiff base complexes are responsible for their high activities in reactions involving high temperatures (Gupta et al., 2009).

Polymer anchored N,N-bis(o-hydroxyacetophenone)ethyleneimidine Schiff base complexes of iron(II), copper(II) and zinc(II) ions show catalytic activity in the oxidation of phenol (Gupta and Sutar, 2008). DNA binding, antitumour activities and micro fluid extraction of viral RNA from infected mammalian cells using cobalt complexes were reported (Kumar et al., 2008; Bhattacharyya and Klapperich, 2008). Cobalt hydroxide nanoparticles modified glassy carbon electrode acts as a biosensor for electrooxidation and determination of some amino acids (Hasanzadeh et al., 2009). Nanoparticles embedded in polymeric cages give rise to interesting applications ranging from nanocatalysis to drug-delivery systems. Cobalt (Co) nanoparticles trapped in polysilvin alcohol (PVA) matrix to yield self-supporting magnetic films in PVA slime. A 20 nm. Co formed in FCC geometry encapsulated with a weak citrate coat when caged in PVA matrix exhibited persistence of magnetism and good radio-frequency response. Cross-linking of PVA chains to form cage-like structures to arrest Co nanoparticles therein, is believed to be the reason for oxide-free nature of Co, promising applications in biomedicine as well as in radio-frequency shielding (Hatamie et al., 2009).

Cobalt(II) complexes were used as catalysts for controlled radical polymerization of number of polar olefins (Lena and Matyjaszewski, 2010). New nano-sized polymer supported Schiff base-cobalt complex catalyst based on cross-linked polycrylamide was synthesized and characterized. The polymeric catalyst showed high efficiency and selectivity in the oxidation of various olefins with environmentally friendly H2O2 as a sole oxidant in aqueous media (Bahman and Soheila, 2011).

Novel zinc coordination polymer with unusual planar hexanuclear zinc unit and tetranuclear zinc(II) metallamacrocycles acting as building blocks show fluorescence properties (Yi-Cheng et al., 2007). Polymer supported zinc complexes were used as clean and recyclable catalysts for trans esterification. They showed a heterogeneous catalytic activity with an easy recyclability on the transesterification of various substrates by methanol at room temperature under the mild and neutral conditions (Yoo et al., 2006).

Ethylenediammonium tris-2,3-pyridine dicarboxylato zinc(II) and coordination polymer of sodium and zinc having (3-oxo-2,3-dihydro-benzo[1,4]oxazin-4-yl)acetate complexes act as catalysts for aldol reactions (Marjit et al., 2011). Grafting of chitosan as a biopolymer onto wool fabric using succinic anhydride shows antibacterial property (Mohammadi et al., 2010). Heterogeneous esterification of cellulose with succinic anhydride was used as a regenerable and powerful sorbent for cadmium removal from spiked high-hardness of ground water (Belhafhafouai et al., 2009).

The present study deals with synthesis and characterization of metal-polymer complexes of cobalt(II) and zinc(II) with poly(3-nitrobenzylidene-1-naphthylamine-co-succinic anhydride).

2. Experimental

2.1. Materials

1:1 novel alternating copolymer poly(3-nitrobenzylidene-1-naphthylamine-co-succinic anhydride) and its copper(II) and nickel(II) complexes were synthesized and characterized in our lab (Dhanaraj and Nair, 2009). All the chemicals used were of AnalR grade. Cobalt(II) and zinc(II) acetates were obtained from Merck. All solvents were purified before use as per the standard procedures (Vogel, 1978). Acetonitrile was dried over phosphorous pentoxide and distilled repeatedly to obtain a highly pure product.

2.2. Synthesis of metal-polymer complex

Metal–polymer complex was synthesized by dissolving the polymer (0.376 g) in THF (1 mmol) and the pH of the solution was adjusted to 7.0 with dilute ammonia. An aqueous solution of cobalt(II) acetate (2 mmol) was added dropwise into the polymer solution with constant stirring. The mixture was then digested on a water bath for 2 h and kept overnight at room temperature. The precipitated metal–polymer complex was filtered, washed with hot distilled water, followed by EtOH and dried at 60 °C in vacuo. A similar procedure was adopted for the preparation of zinc(II) complex using zinc(II) acetate.

2.3. Measurements

The elemental analysis of the polymer and its metal complexes was carried out using a Perkin-Elmer elemental analyzer. The amount of cobalt and zinc present in the metal–polymer complexes was estimated using a titrimetric procedure after decomposing the copolymer. Molar conductance of the metal complexes was measured in DMSO (10−3 M) solution using a coronation digital conductivity meter. 1H NMR spectrum of the zinc(II) complex was recorded in Bruckner 300 MHz NMR spectrometer using CDCl3 as solvent employing tetramethylsilane as the internal standard. The IR spectra were recorded in KBr disc on a JASCO FT/IR-410 spectrometer in the 4000–400 cm−1 region. Electronic spectra were recorded with a Perkin–Elmer Lambda 25 UV–Vis. spectrometer in the 200–900 nm regions. The magnetic moment of cobalt(II) complex was measured by the Gouy method and corrected for the diamagnetism of the component using Pascal’s constants. The magnetic susceptibility values were calculated using the relation, \( \chi_M = 2.83 \left( \frac{Z_m T}{C_0} \right) \) B.M. The paramagnetic nature of the cobalt(II) complex was further confirmed by using EG&G PARC vibrating sample magnetometer. The glass transition temperature was determined by NETZSCH DSC 200 PC. Samples held in sealed aluminium crucibles and the heating rate of 20°C/min under a dynamic nitrogen flow were used for the measurements. Thermal analysis was carried out on NETZSCH STA 409 PC thermal analyzer with a heating rate of 20°C/min using N2 atmosphere. The X-ray diffraction patterns were obtained using Rigaku Dmax X-ray diffractometer with CuKα radiation (\( \lambda = 1.5404 \) Å). SEM images were recorded in a Hitachi SEM analyzer.
3. Results and discussion

The metal–polymer complexes shown in Fig. 1 were found to be insoluble in common organic solvents but sparingly soluble in DMF and DMSO. The low molar conductance data (Table 1) indicate that the metal–polymer complexes are non-electrolytes (Geary, 1971). Elemental analysis data of the metal–polymer complexes are summarized in Table 1. The elemental analysis values are in good agreement with the theoretical values, indicating the metal to polymer ratio to be 1:2.

The $^1$H NMR spectrum of the zinc(II) complex (Fig. 2) shows signals at 4.6, 7.1–7.2 and 7.6–8.1 ppm. In the spectrum of the copolymer the signals for the methylene protons adjacent to the carboxylato group and methylene protons adjacent to the carbonyl group appears, respectively, at 1.2 ppm and 3.5 ppm. Due to the complex formation with zinc, signals for the methylene proton are shifted to 4.6 ppm. The signal for the methine proton appears at 6–6.4 ppm for the copolymer and in the zinc(II) complex, it appears at 7.2 ppm. The signal for the aromatic protons of phenyl and naphthyl groups in the copolymer appears at 6.5–8.8 ppm and it was shifted to a broad band at 7.6–8.1 ppm in the zinc(II) complex.

IR spectra of the cobalt(II) and zinc(II) complexes do not show an absorption band at 1712 cm$^{-1}$ which was present in the copolymer (Table 2). The band at 1653 cm$^{-1}$ observed in the copolymer is shifted to 1639 cm$^{-1}$ for cobalt(II) complex and 1644 cm$^{-1}$ for zinc(II) complex, indicating the coordina-
tion through oxygen of the keto group (Bellamy, 1973; Nakamoto, 1992). The medium intense band at 1173 cm$^{-1}$ due to the C–O stretching frequency of the ester group in the copolymer is shifted to 1179 cm$^{-1}$ for cobalt(II) complex and to 1162 cm$^{-1}$ for zinc(II) complex, indicating the coordination through oxygen of the carboxylato group. The bands at 1527 cm$^{-1}$ and at 1531 cm$^{-1}$ are due to the N'–O stretching of the NO$_2$ group present in cobalt(II) and zinc(II) complexes, respectively. From the IR spectral studies, the disappearance of band or a marked decrease in the band intensity also indicates chelate formation (Koneko and Tsuchida, 1981). It was concluded from these results that both the keto group and the carboxylato oxygen atoms take part in chelation with cobalt(II) and zinc(II).

The electronic spectrum of cobalt(II) complex (Fig. 3) shows only one band in the visible region at 620 nm, which is due to $^4A_2(F) \rightarrow ^4T_1(P)$ transition (Lever, 1984) for the tetrahedral cobalt(II) complexes. This indicates tetrahedral geometry for the present complex. Zinc(II) complex does not exhibit d–d electronic transition due to the completely filled d-orbital. Four coordinate zinc(II) complexes, in general, would have tetrahedral geometry.

For polynuclear systems, the magnetic moment values do not have a fixed range of values characteristic of a particular geometry. It has been reported that (Carlin, 1986; Belanzoni et al., 1996) the exchange interactions arising from the intermetallic bond and through ligands result in intermediate values which do not indicate a geometry type for the polynuclear systems. The higher magnetic moment value of 4.78 BM for present cobalt(II) complex can be attributed to spin orbit coupling which allows mixing in of higher levels for tetrahedral cobalt(II) complex. Thus, the spectral data along with the magnetic moment indicate tetrahedral geometry for the present cobalt(II) complex (Aboaly and Khalil, 2001; Yazici and Akgun, 2006). The magnetic behaviour of the cobalt(II) complex is shown in Fig. 4 in which magnetization (M) is plotted against the applied field (H). The linear fit of M vs H value indicates paramagnetic behaviour for the cobalt(II) complex (Joseph et al., 2005).

From the DSC measurements, glass transition temperature ($T_g$) was taken as the mid point of the transition region. The $T_g$ value of the copolymer is 151.4 $^\circ$C. The reaction of cobalt(II) and zinc(II) with the chelating copolymer increases the glass transition temperature of the metal complexes. The reaction of cobalt(II) with the chelating copolymer increases the glass transition temperature of the metal complex to 254.6 $^\circ$C. The complex shows four exothermic peaks, respectively, at 217.6, 259.9, 295.4 and 335 $^\circ$C. The glass transition temperature of the zinc(II) complex is found to be 153.2 $^\circ$C. The sharp endothermic peak noted at 250.3 $^\circ$C is due to the melting of the complex. The smaller dip in the endothermic curve at 354 $^\circ$C may be attributed to the decomposition of the complex. The higher $T_g$ values for the metal complexes compared to those of the copolymer is due to the decrease in the segmental mobility of the metal–polymer complexes as a result of anchoring of the metal ions in between the chains. The presence of metal atoms or ions in polymer can lead to changes in the physical and chemical properties of the polymers.

Table 2  Infrared spectral data of metal complexes (cm$^{-1}$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(C–O)$_{st}$</th>
<th>(C–N)$_{st}$</th>
<th>(N–O)$_{st}$</th>
<th>(C–O)$_{st}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester</td>
<td>1712</td>
<td>1653</td>
<td>1349</td>
<td>1532</td>
</tr>
<tr>
<td>Ketone</td>
<td>–</td>
<td>1639</td>
<td>1349</td>
<td>1527</td>
</tr>
<tr>
<td>Polymer Co(II)</td>
<td>–</td>
<td>1644</td>
<td>1349</td>
<td>1531</td>
</tr>
</tbody>
</table>

The thermograms of the cobalt(II) and zinc(II) complexes are shown in Fig. 5a and b. The percentage weight loss has also been tabulated and the thermogravimetric data of the metal complexes are shown in Table 3.

The cobalt(II) complex undergoes three stages of decomposition. The first stage of decomposition takes place at 240 $^\circ$C corresponding to 10.5% weight loss. The second stage of
decomposition occurs at 290 °C corresponding to 17.36% weight loss. The third stage of decomposition takes place at 420 °C bringing 40.5% weight loss. The zinc(II) complex undergoes three stages of decomposition. The complex starts to decompose above 200 °C. The first stage of decomposition occurs at 210 °C corresponding to 10% weight loss. The decomposition takes place in the second step at 285.7 °C, bringing a weight loss of 27.5%. At 300 °C, the zinc(II) complex undergoes 32% decomposition. Similar behaviour is observed till 600 °C. The third stage of decomposition occurs at 402 °C, with 45.5% weight loss; 50% weight loss occurs at 460 °C. The above observations indicate that cobalt(II) complex is more stable thermally compared to zinc(II) complex.

The XRD patterns of the metal complexes are shown in Fig. 6a and b. The crystallite sizes of the cobalt(II) and zinc(II) complexes calculated from Scherer’s formula were found to be

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature (°C)</th>
<th>(weight loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>133 (3.4)</td>
<td>311 (87.2)</td>
</tr>
<tr>
<td>Polymer Co(II) complex</td>
<td>240 (10.5)</td>
<td>290 (40.5)</td>
</tr>
<tr>
<td>Polymer Zn(II) complex</td>
<td>210 (10)</td>
<td>285.7 (27.5)</td>
</tr>
</tbody>
</table>

Figure 5  TGA curves of (a) polymer cobalt(II) complex and (b) polymer zinc(II) complex.

Figure 6  XRD pattern of (a) polymer cobalt(II) complex and (b) polymer zinc(II) complex.
micrographs are reported to be observed in zinc oxide materials and needles or fibres. These types of needle and fibre growth were also observed in the copolymer (with out the metal) did not show any preferential growth along one axis. It is speculated that the metal complexes assist to form needles. SEM micrographs of the neat (a) polymer cobalt(II) complex and (b) polymer zinc(II) complex. The needle varies from 50 to 120 μm. It is interesting to note that they also have the tendency to form fibres. The length of the needle decreases with increasing length. The tip of the needle is not well developed. Some portions marked as {x} in the Fig. 7b suggest that they also have the tendency to form fibres. The length of the needle varies from 50 to 120 μm. It is interesting to note that this complex have preferential growth along one axis. It is speculated that the metal complexes assist to form needles. SEM micrographs of the copolymer (with out the metal) did not show any needles or fibres. These types of needle and fibre growth micrographs were observed in zinc oxide materials (Kim et al., 2004).

4. Conclusion

The metal–polymer complexes obtained by the reaction of metal(II) acetate with the copolymer were subjected to various spectral studies. The results showed that the chelation of metal ions can possibly occur between two groups from different polymeric chains. The IR spectral data of the metal-polymer complexes indicate the binding of keto and ester groups of the polymer ligand with the metal ions. Electronic spectrum and magnetic moment studies indicate tetrahedral geometry for cobalt complex. The zinc(II) complex under study also would have tetrahedral geometry. Thermal analysis data showed higher thermal stability and higher glass transition temperatures for cobalt(II) complex compared to the zinc(II) complex. The crystallite sizes of the cobalt(II) complex and zinc(II) complex were found to be 46 nm and 38 nm, respectively, indicating their nanocrystalline nature. The SEM studies show agglomeration of thin flakes for cobalt(II) complex and needle shaped morphological structure for zinc(II) complex.

References