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ORIGINAL ARTICLE

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

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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.

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 interweaving 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

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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)ethylenediamine 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 polyvinyl 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 polyacrylamide was synthesized and characterized. The polymeric catalyst showed high efficiency and selectivity in the oxidation of various olefins with environmentally friendly H_2O_2 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) metallamacrocycle 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 (Belhalfaoui 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 AnalaR 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. ^{1}H NMR spectrum of the zinc(II) complex was recorded in Bruckner 300 MHz NMR spectrometer using $CDCl_3$ 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, $\mu_{eff} = 2.83\ (\chi_m T)$ 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 N_2 atmosphere. The X-ray diffraction patterns were obtained using Rigaku D_{max} X-ray diffractometer with CuKα radiation (λ = 1.5404 Å). SEM images were recorded in a Hitachi SEM analyzer.