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Biologically active and thermally stable polymeric Schiff base and its metal polychelates: Their synthesis and spectral aspects

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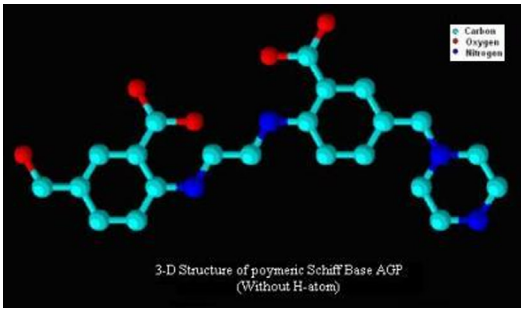
HIGHLIGHTS

- Results obtained, revealed that the synthesized polymers exhibited higher thermal stability than their corresponding ligands.
- Spectral studies confirmed the proposed structure of the metal polychelates.
- Antimicrobial studies show that biological activities of the polymers were enhanced after coordination with the metal.
- Antimicrobial activity and thermal stability of AGP-Cu(II) was the best amongst all synthesized metal polychelates.

GRAPHICAL ABSTRACT



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ABSTRACT

New metal polychelates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) obtained by the interaction of metal acetates with polymeric Schiff base containing formaldehyde and piperazine, have been investigated. Structural and spectroscopic properties have been evaluated by elemental analysis, FT-IR and ^{1}H-NMR. Geometry of the chelated polymers was confirmed by magnetic susceptibility measurements, UV–Visible spectroscopy and Electron Spin Resonance. The molecular weight of the polymer was determined by gel permeation chromatography (GPC). Thermogravimetric analysis indicated that metal polychelates were more thermally stable than their corresponding ligand. All compounds were screened for their antimicrobial activities against *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis*, (bacteria) and *Candida albicans*, *Microsporum canis*, *Cryptococcus neoformans* (fungi) by agar well diffusion method. Interestingly, the polymeric Schiff base was found to be antimicrobial in nature but less effective as compared to the metal polychelates. On the basis of thermal and antimicrobial behavior, these polymers hold potential applications as thermally resistant antimicrobial and antifouling coating materials as well as antimicrobial packaging materials.

Introduction

Continuous efforts have been made to make polymers more stable, increase their mechanical and chemical strengths and to make them durable in the environment. Coordination polymers are usually known for their optical, mechanical and thermal stability [1]. Interest in construction of coordination polymers by linking transition metal ions with polydentate ligands has been constantly growing over the past years [2–4]. In addition to the above discussion, coordination polymers, derived from Schiff base have attractive physicochemical,

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chemical and biological properties, which make them highly processable [5]. Polymeric Schiff base are an important class of coordination polymers with multidentate donor sites, known to form polychelates with transition metal ions. Basic properties of polymeric Schiff base are due to the azomethine linkage in polymeric backbone [6]. They may serve as models in biologically important species, finding applications in biological, clinical, analytical and thermal activities.

Complexation of a metal ion to functional polymeric Schiff base changes its activity due to polymeric effect which has led to a variety of applications. Luminescent properties of polydentate Schiff-base coordination polymers have also been reported [7]. Various works on coordination complexes has revealed that the heterogeneous systems possess more economical potentials and advantages over homogeneous systems [8]. Several metallo-polymers containing metals in the backbone of polymer chain have already been prepared [9,10]. The preparation of polychelates from a polymeric ligand involving anthranilic acid and thiosemicarbazide, thiourea with formaldehyde resin has been reported [11,12]. Salicylidene anthranilic acid possesses antiulcer activity and complexation behavior with copper, increases its antiulcer activity [13]. Antimicrobial activity of coordination polymers depends on the central metal ion as well as nature of the ligand attached along their spatial relationship. So synthesis and structural studies of new compounds of this type have much interest as a first step in search for new Schiff base polymers as potential antimicrobial agents.

Keeping the foregoing facts in mind and in continuation to our research work in this domain, new Schiff base polymers containing transition metal ions in the main chain has been synthesized and their properties have been discussed. Its synthesis represents an attempt to give an organic polymer inorganic functionality.

Experimental

Materials and microbial strains

Anthranilic acid (Merck), 40% Glyoxal (S.D. fine), 35% hydrochloric acid (Merck), Formaldehyde 37–41% (S.D. Fine Chem), Piperazine (Qualingens), transition metal(II) acetates: Manganese(II) acetate tetrahydrate [$Mn(CH_3COO)_2{\cdot}4H_2O$], Cobalt(II) acetate tetrahydrate [$Co(CH_3COO)_2{\cdot}4H_2O$], Nickel(II) acetate tetrahydrate [$Ni(CH_3COO)_2{\cdot}4H_2O$], Copper(II) acetate monohydrate [$Cu(CH_3COO)_2{\cdot}H_2O$], Zinc(II) acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$] (Merck), were used without further purification. Solvents like dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethanol, methanol and acetone (Qualingens) were distilled before use. Microorganisms, *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis*, (bacteria) and *Candida albicans*, *Microsporum canis*, *Cryptococcus neoformans* (fungi) were provided by the culture collection of microbiology laboratory, department of microbiology (A.M.U. Aligarh).

Synthesis

Synthesis of polymeric Schiff base (AGP)

Schiff base of anthranilic acid and glyoxal was synthesized by slightly modified method as described by Kurtoglu et al. [14]. Anthranilic acid (2.74 g, 0.02 mol) was dissolved in 30 mL ethanol then glyoxal (0.58 g, 0.01 mol) was added drop wise at 50 °C with continuous stirring. The reaction mixture was acidified with concentrated HCl and was stirred magnetically under reflux for a day at 60 °C. The formed dark yellow product was dissolved in 25 mL EtOH and left for crystallization at room temperature. Dark brown product was collected, washed with EtOH and dried in vacuum. Yield was 68%.

Elemental analysis for $C_{16}H_{12}N_2O_4$ (296.28 g/mol); *Cal.*: C, 64.86%; H, 4.08%; N, 9.46%. *Obt.*: C, 64.27%; H, 4.14%; N, 9.69%.

FTIR (KBr pellet, cm^{-1}): 3352 (OH), 2931 (=CH—CH=), 3132 (aromatic CH), 1657 (CH=N), 1717 (C=O).

To this synthesized Schiff base (0.01 mol), formaldehyde (0.02 mol) was added in presence of 40 mL DMF and 2–3 drops of conc. HCl. The three necked round bottom flask was equipped with thermometer, condenser and magnetic stirrer. Schematic representation is shown in Scheme 1.

Progress of reaction was monitored by thin layer chromatography. The resulting mixture was heated at 70 ± 5 °C for 1 h with continuous stirring. To this solution 0.86 g (0.01 mol) of piperazine dissolved in 15 mL of DMF was added. After that the reaction mixture was again stirred at 80–90 °C for 24 h. The obtained solution was poured into a beaker and made viscous by vaporizing the excess solvent. Then it was precipitated with an excess amount of cold water. The resulting light brown colored viscous product was washed with distilled water, acetone and diethyl ether. Finally, the product was dried in vacuum desiccators on calcium chloride. The polymeric Schiff base (AGP) was obtained in 62% yield.

Synthesis of metal polychelates

Metal polychelates of [Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] were prepared by using equimolar ratio of polymeric ligand (AGP) and metal(II) acetates. Typical procedure for preparation of metal polychelates of manganese(II) was as follows:

This metal polychelate was prepared by mixing a hot solution of manganese(II) acetate tetrahydrate (2.45 g, 0.01 mol dissolved in 25 mL DMF) with a solution of polymeric Schiff base (0.01 mol dissolved in 25 mL DMF). The reaction mixture was heated at 80 °C for 12 h, with continuous stirring as it becomes sticky and viscous. Brownish yellow product was precipitated by adding ice cooled water. The precipitate was filtered, washed several times with distilled water and acetone, and then dried under vacuum over anhydrous calcium chloride, yield 63%. Same procedure was adopted for the synthesis of other metal polychelates.

Characterization

Elemental analysis for the estimation of percentage of C, H and N present in metal polychelates was carried out by using elemental analyzer system GmbH Vario ELIII. Metal content of metal polychelates was determined by complexometric titration against ethylenediamine tetraacetic acid after decomposition of the complexes with concentrated nitric acid. FT-IR spectra were recorded on a Perkin Elmer IR spectrophotometer (Model 621) using KBr pellets in the range 4000–400 cm^{-1}. Proton NMR spectra was obtained from JEOL GXS 300-MHz FX-1000 Fourier transform NMR spectrometer, taking DMSO-d_6 as solvent and tetramethylsilane as an internal standard. Ultra violet–visible (UV–Vis) spectra were taken on a Perkin Elmer Lambda (EZ-201) spectrophotometer. Magnetic susceptibility was measured on a vibrating sample magnetometer (model 155). Electron Spin Resonance (ESR) of the copper complex was recorded on Varian E112 Xband Spectrometer. The number average (M_n), weight average (M_w), molecular weights were determined by gel permeation chromatography (Shimadzu, Japan) using tetrahydrofuran (THF) as mobile phase and polystyrene as a stationary phase.