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Design and development of several polymeric metal–organic frameworks, spectral characterization, and their antimicrobial activity

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ABSTRACT

Coordination polymers were obtained by the reaction of metal acetates, $M(CH_3COO)_2 \cdot xH_2O$ {where M = Mn(II), Co(II), Ni(II) and Cu(II)} with AFP ligand (AFP = 5,5'-(piperazine-1,4-diylbis(methylene))bis(2-aminobenzoic acid). The AFP ligand was prepared by the one-pot, two-step reaction of formaldehyde, 2-aminobenzoic acid, and piperazine. Structural and spectroscopic properties have been studied by elemental, spectral (FT-IR, ^{1}H NMR, ^{13}C NMR, and UV–vis), and thermogravimetric analysis. UV–vis spectra and magnetic moment values indicate that Mn(II), Co(II), and Ni(II) polymer–metal complexes are octahedral, while Cu(II) and Zn(II) polymer–metal complexes are distorted octahedral and tetrahedral, respectively. The analytical data confirmed that the coordination polymers of Mn(II), Co(II), Ni(II), and Cu(II) are coordinated with two water molecules, which are further supported by infrared spectra and thermogravimetric analysis data. The prepared polymer–metal complexes showed good antibacterial activities against all tested microorganisms; however, the AFP ligand was also found to be effective, but relatively less than their polymer–metal complexes. Along with antibacterial activity, all the polymer–metal complexes exhibit significant antifungal activity against most of the tested fungal strains. The results of antimicrobial activity reveals that the AFP–Cu(II) showed the highest antibacterial and antifungal activity than other polymer–metal complexes.

1. Introduction

The synthesis and characterization of metal complexes with bioactive organic ligands to produce novel potential chemotherapeutic agents is an area of intense chemical research. Of particular note is the pressing need for new antibacterials to replace those losing their effectiveness because of the development of microorganisms' resistance [1]. Thus, the discovery of new antimicrobial agents or increasing the effectiveness of previously known drugs is important [2a–c]. Several polymers with notable antibacterial activity have been synthesized by immobilization of low-molecular-weight antibacterial agents onto the polymers [3]. The controlled aggregation of small coordination complex–based building blocks to form large macromolecules is of great interest in both metal ligand and polyoxometalate chemistry [4]. Particularly, the ability to use both ligand design and adjustment of reaction conditions to understand and control the aggregation processes is crucial. The combination of these approaches yield the best chance of synthesizing sophisticated, potentially

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functional, and biologically active complexes and clusters [5a–d].

In recent years, profound research efforts on the synthesis and characterization of metal-organic coordination polymers has led to significant advances in their electronic, optical, magnetic, and physicochemical properties [6–8]. This includes the search for potential applications of these new materials [9]. There are reports that the transition metal complexes in polymer matrices show interesting chemical and catalytic reactivity toward various small gas molecules. This reactivity has been shown to take place under relatively mild conditions that are different from those of the corresponding free transition metal complexes or those in inorganic oxide-supported systems [10–12]. The characterization of transition metal ion–containing polymers has been the subject of numerous investigations. It has been demonstrated that the thermophysical properties of ligands can be modified by coordination to transition metal ions [13–15]. In the present study, a novel AFP ligand whose 3-D molecular structure is given in Fig. 1 is reported. The structure is drawn using ChemBioDraw Ultra 13. The article describes the synthesis and characterization of the AFP ligand and its polymer–metal complexes containing Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) metal ions. Moreover, the AFP ligand and their polymer–metal complexes were also screened toward two kinds of organisms i.e. fungus and bacterium for their antimicrobial evaluation [16].

2. Experiment

2.1. Materials and strains

Piperazine (S D Fine-Chem Ltd.), 2-aminobenzoic acid, formaldehyde (37% aqueous solution), sodium hydroxide (Merck), and $M(CH_3COO)_2 \cdot xH_2O$, where M = Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) and x = 1,2,4 (Qualigens fine chemicals) were used without further purification. Solvents such as acetone, methanol, diethyl ether, dimethyl formamide (DMF), dimethylsulfoxide (DMSO) (S D Fine-Chem Ltd.), and ethanol (Jiangsu Hauxi International) were purified by standard procedures before use. All the microorganisms were provided by the Culture Collection Center of Microbiology laboratory, Department of Microbiology (AMU, Aligarh).

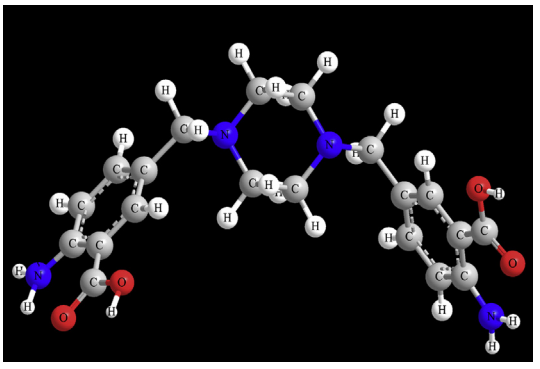

Fig. 1. Energy minimized cylindrical bonded 3-D molecular structure of the AFP ligand.

2.2. Synthesis of AFP ligand

2-aminobenzoic acid (0.01 mol) and formaldehyde (0.01 mol) in 1:1 M ratio were transferred to a 250 ml three-necked round bottom flask equipped with thermometer, condenser, and magnetic stirrer containing DMF (~50 mL) as a solvent, and the pH was adjusted in alkaline range with 40% aqueous NaOH. The reaction mixture was stirred magnetically at temperature up to 80°C for 3 h. A piperazine solution (0.01 mol) in 25 mL DMF was added to this system and stirred again for about 1 h up to 90–115°C. The progress of reaction was monitored by thin layer chromatography (TLC). The reaction mixture was cooled and precipitated using a 50/50 (v/v) water/acetone mixture. The obtained solid which is light brown in color (AFP–ligand) was filtered, and re-precipitated from DMF and ethanol. It was then filtered and washed repeatedly with distilled water and acetone and dried in a vacuum oven to remove the solvent (DMF and ethanol), yield 82% (2.05 gm).

2.3. Synthesis of polymer–metal complexes of AFP

A series of polymer–metal complexes [Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] were prepared by using equimolar ratio (1:1) of AFP ligand and metal acetates. A typical synthesis of polymer AFP–Mn(II) is as follows.

The AFP ligand (3.84 gm, 0.01 mol) was dissolved in DMF (20 mL). Mn(II) acetate tetrahydrate (2.45 gm, 0.01 mol) was also dissolved in a minimum quantity of hot DMF (25 mL). Both the solutions were mixed and heated at reflux at 75°C with constant stirring. The resulting viscous dark brown colored product was precipitated by pouring it into excess of distilled water. The AFP–Mn(II) complex gets precipitated, and it was filtered and washed several times with water and acetone and dried at room temperature, yield 76%. Similar procedures were adopted for the synthesis of other polymer–metal complexes.

2.4. Measurements

The elemental analysis of carbon, hydrogen, and nitrogen were carried out on a Perkin–Elmer model-2400 elemental analyzer. The metals were determined by complexometric titration against EDTA after decomposing with concentrated nitric acid. The solubility of ligand and their polymer–metal complexes were investigated in different solvents at room temperature. The IR spectra were recorded on a PerkinElmer infrared spectrometer model 621 using KBr pellets. ^{1}H NMR spectra were recorded on a JEOL-FX-100 FT-NMR instrument in dimethylsulfoxide (DMSO-d_6) solution with tetramethylsilane as an internal standard. The thermal stability of ligand and their polymer–metal complexes were evaluated with a TA analyzer 2000 at a heating rate of 20°C/min under nitrogen. The electronic spectra of the polymer–metal complexes were recorded on a PerkinElmer Lambda-201, and magnetic susceptibility measurements were carried out with vibrating sample magnetometer. The antimicrobial activity of the ligand and

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