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Synthesis and characterization of some arylhydrazone ligand and its metal complexes and their potential application as flame retardant and antimicrobial additives in polyurethane for surface coating

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ABSTRACT

Hydrazones are versatile organic ligands and can be synthesized by condensation of hydrazides with carbonyl compounds (aldehydes/ketones). These compounds coordinate to the metal ions via azomethine nitrogen. Hydrazone Schiff's base ligands and their transition metal complexes possess a number of biological and flame retardant applications. Some selected divalent metal (Cu^{II} and Ni^{II}) complexes of hydrazone Schiff base ligand, namely o-methoxybenzaldehyde benzoylhydrazone (MBH) was synthesized and fully characterized by elemental analysis, FTIR, ^{1}HNMR and mass spectra. This work summarizes the application of the prepared MBH ligand and its metal complexes. The prepared MBH ligand and its metal complexes were physically incorporated in polyurethane coating and evaluated for their flame retardancy and antimicrobial activity for surface coating. The flame retardancy of these materials was characterized by the limiting oxygen index (LOI) test. The antimicrobial activity of these materials was screened against Gram-positive bacteria, Gram-negative bacteria and fungi. The physical, mechanical and chemical properties were studied to ascertain any drawbacks. On the basis of experimental results of an oxygen index (LOI) and the biological activity, the synthesized MBH ligand and its metal complexes showed excellent flame retardancy and antimicrobial activity. In addition, the metal complexes were much more active than the original MBH ligand. Quantum chemical calculations were also performed by Semiempirical PM3 method to find the optimum geometry of the ligand and its metal complexes. The calculated pharmacokinetic parameters in silico, showed promising futures for application of the MBH ligand and its metal complexes as high antimicrobial potency agents.

1. Introduction

Polymers such as polyurethane, polyester, and polyesteramide are susceptible to microbial attack, when they are exposed to the atmosphere or used as an adhesive or a coating material [1–4]. Generally, microorganisms have been found to cause dis-bonding and blistering of coatings under various service conditions [5–7]. Paint formulations traditionally containing biocidal species, are used to protect the coating surface from microbial attack [8]. Up until the end of 1990's, the most effective anti-fouling paints were based on organotin compounds, mostly tributyltin compounds (TBT-based paints). TBT and its derivatives were found to be harmful molecules to marine eco-systems by Alzieu [9]. Thus, TBT-based paints were completely prohibited by 1 January 2008 [10,11] and as a consequence promoted research into new ecological paints. Modification of polyurethanes by the incorporation of metal and Schiff base metal complex was found to enhance polyurethanes antimicrobial activity, flame retardancy and the thermal stability [12]. Jayakumar et al. had synthesized several petrobased transitional metals contained polymers from divalent transition metal salts, these polymers have been found application as antibacterial coatings [5,6,13–16]. Hydrazones are versatile ligands occupied a

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central role in the development of coordination chemistry. This feature comes from the fact; they are potential poly nucleating ligands possessing azomethine, amide, phenol or methoxy functions which offer varying bonding possibilities in metal complexes. Studies of metal chelates of hydrazone derivatives have been recognized [17]. Moreover, the biological activity of complexes derived from hydrazones has been widely studied and contrasted, acting in processes such as antibacterial, antitumoral, antiviral, antimalarial and antituberculosis effects [18–20]. The most studied among benzoylhydrazones are the benzoylhydrazones of salicylaldehyde or its substituted, which hesitate in their coordination with the metal ions forming a five or six chelate ring around the central metal. Indeed, several metal complexes of benzoylhydrazones of salicylaldehyde, substituted-salicylaldehyde and 2-hydroxynapth-1-aldehyde have been extensively studied [21–23]. Actually the investigation of new antimicrobial agents is important; in this regard heterocyclic bases have great importance in biological and industrial fields. In view of the importance of hydrazones and their chelates, we have undertaken the synthesis and structural characterization studies on o-methoxybenzaldehyde benzoylhydrazone (MBH) ligand and its bivalent (Cu, Ni) metal complexes. The objective of this investigation is to establish whether the MBH ligand and its metal complexes have a role in enhancing the flame retardancy and antimicrobial activity properties of the polyurethane coating.

2. Experimental

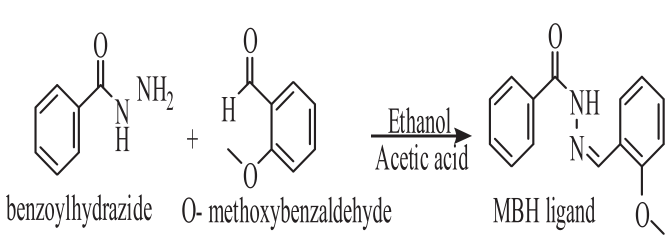
2.1. Materials

All the chemicals used during the research project were sourced internationally, or from local companies, and were of pure grade quality.

2.2. Methods and techniques

2.2.1. Synthesis of o-methoxybenzaldehyde benzoylhydrazone (MBH) ligand

Benzoylhydrazide (BH) was prepared following the method described in the literature [24,25]. The MBH ligand used in this research work was prepared in a similar manner according to the reported procedure [26] as given. Benzoylhydrazide (3.0 g, 0.022 mol) was dissolved in absolute ethanol (50 ml) and the resulting solution was then added to an ethanolic solution (50 ml) of o-methoxybenzaldehyde (2.99 g, 0.022 mol). The reaction mixture was prolonged under reflux for 2 h in the presence of 2 ~ 3 drops glacial acetic acid. The separated product was filtered, washed with ethanol, crystallized using ethanol and finally dried in oven at 80 °C for 24 h. The resulting ligand has the chemical formula $C_{15}H_{14}N_2O_2$ as shown in Scheme 1. The authenticity of the ligand was proved by elemental analyses, mass, FTIR and ^{1}HNMR spectroscopy. The synthesized hydrazone (MBH) ligand is insoluble in petroleum ether and soluble in most common organic solvents, e.g. alcohol, acetone, benzene, chloroform, DMF and DMSO.



Scheme 1. Synthesis of o-methoxybenzaldeyhde benzoylhydrazone (MBH) ligand.

2.2.2. Synthesis of the metal complexes of MBH ligand

All the isolated solid complexes were prepared by mixing equimolar amounts of MBH ligand and metal (II) acetates [M = Cu (II) and Ni (II)] in 100 ml ethanol. The reaction mixture was refluxed on hot plate for 3 h. Colored microcrystalline solids were isolated by concentrating the solutions to their halves and then filtered on hot. The obtained complexes were washed repeatedly with hot ethanol and finally dried in oven at 80 °C for 24 h. The complexes retain their colors for a long time, insoluble in water and petroleum ether, and soluble in DMF and DMSO.

2.3. Characterization studies

The physical measurements were carried out using the methods and appliance models reported earlier [27] as follows. The elemental analysis for carbon, hydrogen and nitrogen was performed on Perkin Elmer 2400. Metal contents (wt. %) was estimated complexometrically by EDTA using xylenol orange as an indicator and solid examine as a buffer (pH = 6). FTIR spectra of the ligand as well as the complexes were recorded as KBr pellet on a Bruker Vector 22, single beam spectrometer at a spectral resolution of 2.0 cm^{-1}. The ^{1}HNMR spectra were recorded on a Varian Mercury VX300 MHz spectrometer at 25 °C using DMSO solvent and TMS as an internal standard. Mass spectra of the MBH ligand was recorded on the Shimadzu-GCMS-Q5050 instrument using the direct inlet system.

2.4. Preparation of polyurethane coating films containing MBH ligand and its metal complexes for surface coating

The polyurethane coating compositions were prepared by means of incorporating o-methoxybenzaldehyde benzoylhydrazone (MBH) ligand and its metal complexes, in the ratio of 1.0, 1.5 and 2.0 wt. %, into polyurethane coating. The composition of the polyurethane coating is tabulated in Table 1. The samples of different molar ratio were then applied to both steel and glass panels by means of a brush. All efforts were made to maintain a uniform film thickness of 100 ± 5 μm for evaluating the physical and mechanical properties.

2.5. Flame retardant testing method

The performance of polyurethane coating incorporated MBH ligand and its metal complexes as a flame retardant additives was evaluated in a limiting oxygen index (LOI) chamber. LOI values can be determined by standardized tests such as ASTM D: 2863-06, ISO 4589-1: 1996, DIN 4102-B2 and NF T51-071 procedures. This test method was first proposed in 1966 by Fenimore and Martin [28].

Table 1
Polyurethane coating composition.

Component	wt. %
Refined sunflower oil	33.42
Glycerol	0.039
Litharge (lead oxide catalyst)	0.03
Pentaerythritol	4.61
Turpentine	47.30
Mixed drier	2.37
Toluene diisocyanate	11.37
UV absorber	0.26
Anti skinning agent	0.32
MBH ligand and its metal complexes	1.0–2.0

Viscosity: G-I (Gardner), color: 3 (Gardner), solid content: 53 ± 2%.