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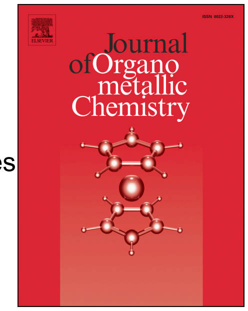

Synthesis and characterization of some arylhydrazone ligand and its metal complexes and their potential application as flame retardant and antimicrobial additives in polyurethane for surface coating

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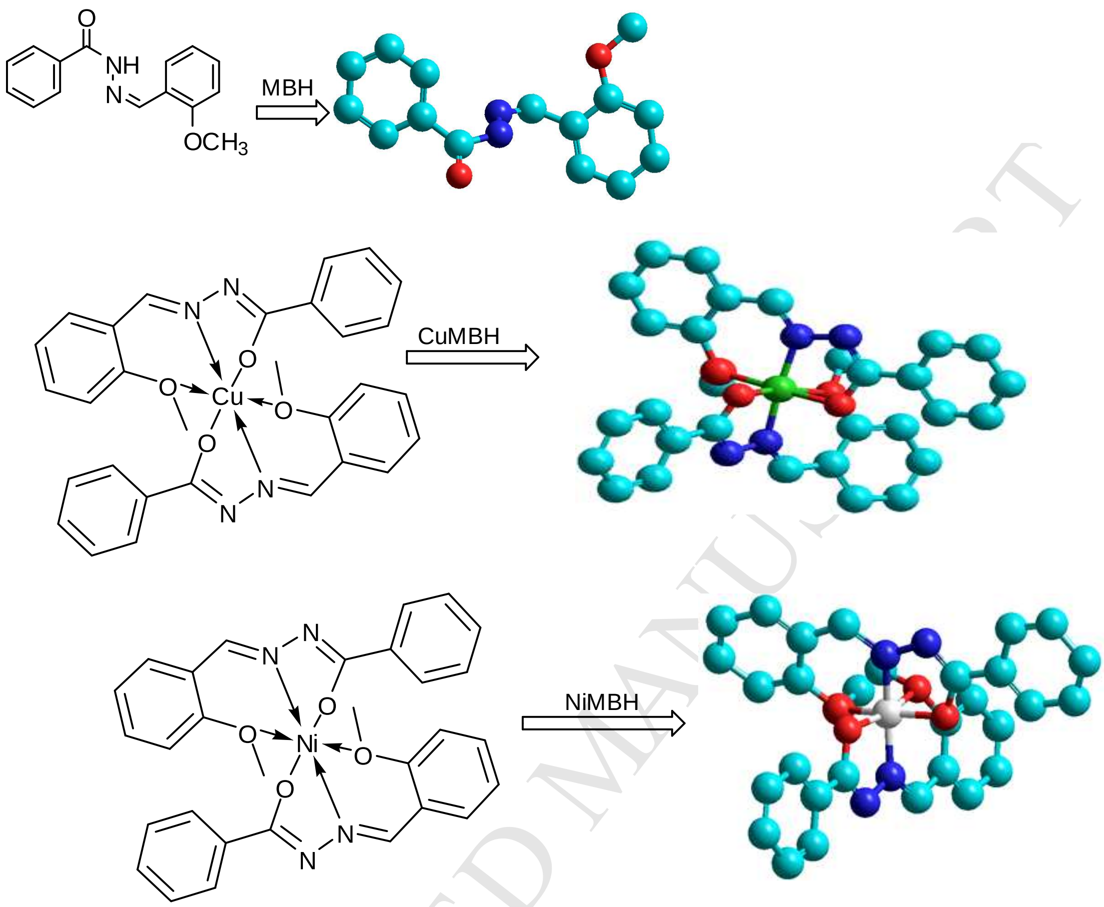
Graphical abstract synopsis

The MBH ligand and its metal complexes showed excellent flame retardancy and antimicrobial activity. The metal complexes were much more active than the original ligand. The molecular modeling study revealed that molecular properties of MBH ligand and its metal complexes are biologically safe, active and fulfill Lipinski's rule of five.

Graphical abstract –pictogram



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.

Keywords: Hydrazones; Schiff base ligand; antimicrobial activity; flame retardant activity; molecular modeling; polyurethane coating.

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 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 mole) 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 mole). 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.

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 ^{o}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 $^{\circ}$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 ±5μm 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]. Test panels were prepared using a combustible material (wood specimen). It was important that the panels were free of any surface contamination, or imperfections, prior to the coating application. Hand tool cleaning (sand paper) was carefully used to treat the faces and edges of the panels. Final dry film thickness (DFT) was 100 ± 5µm. In all cases, the film application was applied by means of brushing. Following 10 days of air drying, the panels under study were heated at 50-60°C for 2h to eliminate any remaining solvent.

2.6. Antimicrobial testing method

The synthesized MBH ligand and its metal complexes were screened for their antimicrobial activity against eight different test organisms having environmental and clinically importance. The microorganism`s inoculums were uniformly spread using a sterile cotton swab on a sterile Petri dish Malt agar (for fungi) and nutrient agar (for bacteria). 100 µL of each sample was added to each well (10 mm diameter holes cut in the agar gel, 20 mm apart from one another). The systems were incubated for 24-48 h at 37 °C (for bacteria) and at 28 °C (for fungi). After incubation, microorganism growth was observed. Inhibition of the bacterial and fungal growth were measured in mm. Tests were performed in triplicate.

2.7. Physical and mechanical testing of films

A variety of physical and mechanical evaluations of the coating films were carried out according to appropriate ASTM standard test methods. These included the preparation of the steel panels (ASTM D: 609-00), measurement of film thickness (ASTM D:1005-07), the degree of gloss for individual coating film (ASTM D: 523-08), film hardness by pencil test (ASTM D: 3363-00), adhesion ‘cross hatch test’ (ASTM D: 3359-02), flexibility ‘bend’ test (ASTM D: 522-08) and resistance to mechanical damage ‘impact resistance’ (ASTM D: 2794-04).

2.8. Molecular modeling studies

The conformational analysis of the target compounds has been performed using the Merck molecular force field MMFF94 [29] (calculations in vacuo, bond dipole option for electrostatics, Polake Ribiere algorithm, RMS gradient of 0.01 kcal/mol) and then implemented in MOE [30]. The most stable conformer was fully geometrical optimized with (PM3) semi-empirical *Hamiltonian* molecular orbital calculation MOPAC-7 package [31]. The obtained electronic structural and pharmakinetic parameters, such as, total energy, electronic energy, heat of formation, the dipole moment of the molecules, the energy of the highest occupied molecular orbital, the lowest unoccupied molecular orbital, total polar surface area, absorbance percentage, lipophilicity, solubility, hydrogen bond acceptor, hydrogen bond donor, and the molar refractivity was recorded.

3. Results and discussion

3.1. Synthesis and instrumental analysis of MBH ligand and its metal complexes

The chemical structure of the prepared MBH liagnd and its metal complexes are represented in Scheme 1 and Figs.1-2. Elemental analysis and product color of the prepared MBH ligand and its metal complexes were measured and listed in Table 2. The good agreement between the experimental and theoretical values of the C, H, N and M levels reveals that the methods of synthesis and purification of the products were performed successfully.

3.2. Spectral analysis of MBH ligand and its metal complexes

The positions of the significant FTIR bands of the prepared MBH ligand as well as its metal complexes are summarized in Table 3. The FTIR spectra of the free MBH ligand exhibit strong absorptions at 3188, 1643, 1606 and 700-800 cm^{-1} assignable to υ (NH), υ (C=O), υ (C=N) and the out of plane deformation of the aromatic ring, respectively. The observation of the (C=N) band ascertains the formation of the azomethine linkage and thus the requested hydrazones. The positions of other bands assigned to $\upsilon(CH)_{aromatic,\ aliphatic}$ and $\delta(NH)_{amide}$ are observed at

3028, 2950 and 1252 cm^{-1} respectively. The position of bands assigned to the metal complexes is demonstrated in Table 3. Finally, the persistence of new bands attributed to υ (M-O) and υ (M-N) supports the formation of the metal complexes. The authenticity of the prepared o- methoxybenzaldehyde benzoylhydrazone (MBH) ligand was proved by ^{1}HNMR spectra as shown in Fig. 3, it was measured in DMSO-d_6 solvent and showed three signals with integration (1:1:3). The signal at δ= 11.9 ppm is assigned to (-NH-, s), the signal at δ= 8.8 ppm is assigned to azomethine (-CH=N-, s) and at δ= 3.9 ppm (-OCH_3, s). The multiple (m) signals attributed to the aromatic protons were observed within 6.5-8ppm with slight change in their positions.

3.3. Evaluation of coating film properties

3.3.1. Evaluation of MBH ligand and its metal complexes as a flame retardant additive incorporated physically into polyurethane coating

It is clear that the incorporation of MBH ligand and its metal complexes into polyurethane coating, in the ratio's mentioned in the experimental section, results in enhanced flame retardancy when compared to blank polyurethane coating. This is as a result of the fact that, the incorporation of azometine (-CH=N-) linkage in the polyurethane improved the thermal stability, the introducing of aromatic ring which has a stabilizing effect against thermal degradation that result in improved flame retardant and the introducing of nitrogenous compounds provide superior flame retardant properties. The results obtained from the LOI test are shown in Table 4 and Fig. 4. It can be observed, that the LOI value of the blank polyurethane coating is 20 and the maximum LOI with Ni-MBH present is 29. Normal atmospheric air (i.e. The air that we inhale) contains approximately 21% oxygen, so a material with a LOI less than 21% would burn easily in air. In comparison, a material with a LOI value greater than 21%, but less than 27%, would be considered to be 'slow-burning'. However, a self-extinguishing material is one that has a LOI greater than 27% and this would stop burning after the removal of the fire, or the ignition source [32]. An interesting point associated with the results is that the LOI curves for the MBH ligand and its metal complexes are more or less linear. A further interesting point is that the LOI values of metal complex Ni-MBH is higher than the metal complex Cu-MBH, this may be attributed to the higher melting point of nickel metal and its metal complex than the corresponding copper metal and its complex. The obtained results also indicated that the flame retardancy increases with the increase in the metal complex addition level.

3.3.2. Evaluation the antimicrobial activity of MBH ligand and its metal complexes as a biocide additive incorporated physically into polyurethane coating

The biocide additives are commonly used to prolong the life of surface coatings. They prevent, or slowdown, the growth of organisms on the coating surface. Hydrzone ligands have a good potential application as an antimicrobial. The antimicrobial activities of the prepared MBH ligand and its metal complexes were evaluated against two Gram- positive bacteria (Staphylococcus aureus and Bacillus subtilis), two Gram-negative bacteria (Pseudomonas aeruginosa and Escherichia coli) and four fungi (Aspergillus fumigates, Penicillium italicum, Syncephalastrum racemosum and Candida albicans). The activity was tested by a disc-diffusion method. . The results obtained from the anti-microbial activity are shown in Table 5. The prepared MBH ligand and its metal complexes exhibited antimicrobial activity, they are azomethine derivatives, the azomethine (-CH=N-) linkage is essential for biological activity, several azomethine has been reported to possess remarkable antibacterial and antifungal activity. In addition the biological activity of this ligand and its metal complexes are due to the fact that; the aromatic ring present in their structures is a constituent of many biological systems. The MBH ligand showed little better effect on Gram- positive than on Gram- negative bacteria. The results also indicated that the metal complexes were more effective than the original MBH ligand. It has been reported that metal complexes have higher antibacterial activity than that of free ligand. The metal complexes of copper and nickel showed the highest effect on Gram- positive and negative bacteria and also Fungi. The results also illustrated that the prepared ligand and its Ni-MBH metal complexes have a lower effect on fungi than the Cu-MBH metal complex. The obtained results also indicated that the antimicrobial activity against the target microorganisms increases with the increase in the metal complex addition level.

3.3.3. Evaluation the effect of MBH ligand and its metal complexes on the physical and mechanical properties of polyurethane coating

The effect of incorporating MBH ligand and its metal complexes into the polyurethane coating was evaluated using a variety of standard test methods for gloss, hardness, adhesion, flexibility and impact strength. These test methods were utilized to determine any negative aspects that might occur due to the incorporation of MBH ligand and its metal complexes physically into polyurethane coating. The physical and the mechanical characteristics of polyurethane coating are presented in Table 6. Firstly, all films of polyurethane coating compositions gave a very clear, transparent and homogeneous appearance.

(a) Gloss: This was measured using a Sheen UK glossmeter. On observing the films using a 60° angle, it could be seen that the MBH ligand and its metal complexes additives actually increased slightly the gloss level. This is obviously a positive result which may be attributed to the introduction of aromatic rings, present in the additive structure. In addition, metals incorporation in the polymer is known to enhance their gloss [13].

(b) Scratch hardness test: This was determined by using a Sheen UK hardness tester. The scratch hardness is observed to vary between 1.4 and 2.0 kg for all coating films. It is clear from the data that the MBH ligand does not affect on the scratch hardness of the coating film, while Ni-MBH metal complex showed the highest hardness; this may be attributed to the fact that, the nickel metal possesses higher hardness than the copper metal.

(c) Cross hatch adhesion & flexibility test: The cross hatch adhesion and flexibility (bending) test show that, the film for all the coating compositions passed the adhesion and Mandrel bend test, with no obvious significant change being observed for the incorporation of MBH ligand and its metal complexes in polyurethane coating.

(d) Resistance to mechanical damage (impact resistance): This was measured using a Sheen UK impact tester. The impact resistance of the coating on the steel panels was tested by means of dropping a 890 g steel ball from a height of 1 m. It is clear from the data that the MBH ligand does not affect on the impact resistance of the coating film. The impact strength was shown to increase in the presence of the MBH metal complexes and Ni-MBH showed the highest results.

3.3.4. Evaluation the effect of MBH ligand and its metal complexes on the chemical properties of polyurethane coating

The effect of incorporating MBH ligand and its metal complexes into the polyurethane coating towards the chemical resistance was undertaken using glass panels (25 mm x 75mm). The coated glass panels were sealed, using paraffin wax at the edges, and immersed to half their length in each individual test solution: (i) 5.0 wt. % anhydrous sodium carbonate, (ii) 10.0 wt. % sulphuric acid and (iii) 1:3 by volume benzene/mineral turpentine solvent mixture. The panels were then removed from the individual test solution, wiped carefully and then allowed to dry at room temperature, prior to assessment of any change. The obtained data indicated that the chemical resistance of polyurethane coating was not significantly changed by the addition of MBH ligand and its metal complexes.

3.4. Molecular modeling studies

3.4.1. Geometrical conformation

In trying to achieve better insight into the molecular structure of MBH ligand and its metal complexes, the conformational analysis of the target compounds has been performed in (PM3) semi-empirical Hamiltonian molecular orbital calculation using MOE [30]. The possibility exists of the prepared MBH ligand in two stereoisomer forms are shown in Fig. 1, the minimal optimal energy at PM3 were calculated to prefer the most stable stereoisomer is shown in Table 7, which showed that, the most stable stereoisomer MBH ligand is *(Z)* form; this may be explained by the presence the intra-molecular hydrogen bond interaction of H-NH fragment with the O atom of carbonyl moiety, which owing to slightly reduce its calculated energy. Other evidence supported this explanation, the $N_{PhC=N}$ atom with sp^2 hybrid orbital has more s-character, and the maximum of the electron density is closer to the nuclei compared with the electron density distribution at sp^3 hybridized N_{N-N} and N_{N-CH} atoms, which leads to lengthening the bonds of PhC—N bonds. Furthermore, The geometry optimization of M-MBH structures were stabilized by arranging four phenyl rings in coplanar position with each other in all complexes, which arranged at the same time in perpendicular to the plane of metal rings as shown in Fig. 2. The bond lengths of all the active groups taking part in coordination are longer than that already exist in the ligand. All bond angles in complexes are quite near to a tetrahedral geometry predicting sp3d2 hybridization. The higher HOMO energy values indicate that the molecule is a good electron donor, yet on the other hand, the lower HOMO energy values indicate a weaker ability of the molecules for donating an electron. LUMO energy is an indication of the ability of a molecule to receive electrons [29].

3.4.2. ADMET factors profiling

The Pharmacokinetic parameters were playing an important role in the development of bioactive molecules. Many potential bioactive molecules fail to reach for application trial, because of ADMET (absorption, distribution, metabolism, elimination and toxic) Factors. Therefore, a computational study was performed for prediction the ADMET properties of the MBH ligand and its metal complexes by determination of topological polar surface area (TPSA), a calculated percent absorption (%ABS) which was estimated by Zhao et al. equation [33], and ‘‘rule of five’’ formulated by Lipinski [34], which established that, a chemical compound could be an bioactive, if no more than one violation of the following rule: factor of the lipophilicity (Log p < 5), number of hydrogen bond donor sites (HBD ≤ 5), number of hydrogen bond acceptor sites (HBA ≤ 10), molar refractivity (mr, 40-130). In addition, the total polar surface area (TPSA) is another key property linked bioactive molecule, the passively absorbed molecules with (TPSA<140) has low oral bioavailability [35]. All calculated descriptors were performed using MOE Package [30]. Our results shown in Table 8 revealed that, the factor of the lipophilicity (Log p) [36] was less than 5.0, number of hydrogen bond donor sites (2-4), number of hydrogen bond acceptor sites (4-6), molar refractivity (107.75- 116.33) and total polar surface area (65.1-67.8) which fulfill Lipinski’s rule. In addition the absorbance percentage of MBH ligand was higher than its metal complexes. The HOMO and LUMO of a molecule play important roles in intermolecular interactions [37], through the interaction between the HOMO of the drug with the LUMO of the receptor and vice versa. The interactions were stabilized inversely with energy gap between the interacting orbits. Increasing HOMO energy and decreasing LUMO energy in the molecule lead to enhancement stabilizing interactions, and hence, binding to the receptor. The obtained results showed that, Cu-MBH have lowest energy gap (8.84 eV) which explained its highest antimicrobial affinity.

4. Conclusions

In this study Cu and Ni complexes of hydrazone Schiff base ligand, namely o-methoxybenzaldehyde benzoylhydrazone (MBH) derived from condensation of benzoylhydrazide and o- methoxybenzaldehyde was synthesized and characterized. The MBH ligand and its metal complexes were incorporated physically into a polyurethane coating to study their antimicrobial and flame retardant properties. The study showed that, the activity order of the synthesized ligand and its metal complexes against microorganism can be represented as Cu-MBH > Ni-MBH >MBH ligand. In general the metal complexes show higher activity than the free ligand against the same organism under identical experimental conditions. This improvement may be attributed to the presence of azomethine linkage, which possesses biological activity, in addition to the presence of metal. However, the flame retardant activity order can be represented as Ni-MBH > Cu-MBH > MBH ligand. This improvement may be attributed to the introducing of high molecular weight nitrogenous compound, introducing aromatic ring and introducing of metals with high melting point. The obtained results also indicated that the antimicrobial activity against the target microorganisms and the flame retardant properties increases with the increase in the metal complex addition level. The results obtained, indicate that the mechanical properties were slightly improved with an increase in the metal complex content within the polyurethane. However, chemical resistance was not significantly changed by the addition of MBH ligand and its metal complexes. Also, the molecular modeling was studied and this revealed that molecular properties of MBH ligand and its metal complexes are biologically safe, active and fulfill Lipinski's rule of five. The final result may give a promising approach for using such compounds in the future as a diverse range of applications due to its simple synthesis, high potent antibacterial, antifungal and flame retardant agent at low concentrations.

Conflict of Interest: The authors declare that they have no conflict of interest.

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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%

Table 2

Physico – chemical properties of o- methoxybenzaldehyde benzoylhydrazone (MBH) ligand and its metal complexes.

Characteristics		MBH	Cu-MBH	Ni-MBH
Color		White	Brown	Green
M.p (^{O}C)		200	>220	>280
Mass	Calcd.	254.3		
	Found	254		
Elemental analysis				
C %	Calcd.	70.84	63.20	63.72
	Found	70.61	63.51	63.55
H %	Calcd.	5.56	4.91	4.96
	Found	5.82	4.99	4.99
N %	Calcd.	11.02	9.83	9.91
	Found	11.60	9.32	9.26
M %	Calcd.	-	10.88	10.09
	Found	-	10.40	10.10

Table 3

IR absorption data of o- methoxybenzaldehyde benzoylhydrazone (MBH) ligand and its metal complexes.

Compound	ν(NH)	ν(C=O)	ν(C=N)	ν(CH) aromatic	ν(CH) aliphatic	δ(NH)	νM-O/M-N
MBH	3188	1643	1606	3028	2950	1252	-
Cu-MBH	-	-	1599,1616	3052	2950	-	537/447
Ni-MBH	-	-	1598,1610	3020	2948	-	533/446

Table 4

Flame retardant characteristics of polyurethane coating incorporated MBH ligand its metal complexes as a flame retardant additives.

Formulation	Additive wt.%	Limiting oxygen index (LOI)
Blank polyurethane	-	20
MBH ligand	1.0	21
	1.5	22
	2.0	23
Cu-MBH	1.0	23
	1.5	25
	2.0	26
Ni-MBH	1.0	24
	1.5	27
	2.0	29

Table 5

The antimicrobial screening activity of polyurethane coating incorporated MBH ligand and its metal complexes as a biocide additive.

Microorganisms	Blank polyurethane	MBH wt.%			Cu-MBH wt.%			Ni-MBH wt.%		
		1.0	1.5	2.0	1.0	1.5	2.0	1.0	1.5	2.0
Staphylococcus aureus	-ve	+ve	+ve	++ve	++ve	+++ve	+++ve	+ve	++ve	++ve
Bacillus subtilis	-ve	+ve	+ve	+++ve	++ve	+++ve	+++ve	+ve	++ve	++ve
Pseudomonas aeruginosa	-ve	-ve	+ve	++ve	++ve	++ve	+++ve	+ve	++ve	+++ve
Escherichia coli	-ve	-ve	+ve	++ve	++ve	+++ve	+++ve	+ve	++ve	++ve
Aspergillus fumigates	-ve	-ve	+ve	++ve	++ve	++ve	+++ve	+ve	++ve	++ve
Penicillium italicum	-ve	-ve	+ve	++ve	++ve	++ve	+++ve	+ve	++ve	++ve
Syncephalastrum racemosum	-ve	-ve	+ve	+++ve	++ve	+++ve	+++ve	++ve	++ve	+++ve
Candida albicans	-ve	-ve	+ve	+ve	+ve	++ve	+++ve	+ve	+ve	++ve

Where, Inactive = -Ve,

Mildly active: Inhibition values = 0.1–0.6 cm beyond control = +

Moderately active: Inhibition values =0.65–1.0 cm beyond control =++

Highly active: Inhibition values = 1.1–1.5 cm beyond control =+++

Table 6

Physical and mechanical characteristics of polyurethane coating incorporated MBH ligand and its metal complexes.

Formulation	Additive wt. %	Gloss at 60°C	Hardness (Kg)	Adhesion	Flexibility	Impact (J)
Blank polyurethane	-	80	1.4	5B	Pass	1.6
MHB ligand	1.0	82	1.4	5B	Pass	1.6
	1.5	82	1.4	5B	Pass	1.6
	2.0	80	1.4	5B	Pass	1.6
Cu-MBH	1.0	84	1.6	5B	Pass	1.7
	1.5	87	1.6	5B	Pass	1.9
	2.0	89	1.8	5B	Pass	2.0
Ni-MBH	1.0	87	1.6	5B	Pass	1.8
	1.5	89	1.8	5B	Pass	2.0
	2.0	89	2.0	5B	Pass	2.2

Table 7

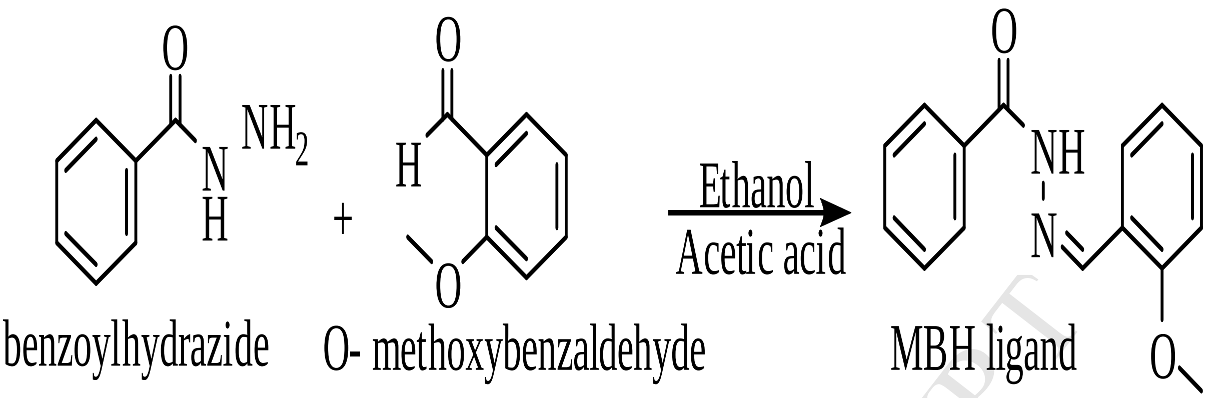
The calculated energies at PM3 molecular orbital for compound stereoisomers of MBH ligand and its metal complexes.

Symbol	Parameter (unit)	E- MBH	Z- MBH	Cu-MBH	Ni-MBH
E	The total energy (Kcal/mol)	-73844.4	-80383.5	-89965.8	-87590.4
Eele	Electronic energy (Kcal/mol)	-519760	-526471	-793513	-532050
HF	Heat of formation (Kcal/mol)	-9.8148	-10.362	-312.53	-280.023
HOMO	Highest Occupied Molecular Orbital (eV)	-9.3471	-8.9961	-7.97	-6.99
LUMO	Lowest Unoccupied Molecular Orbital (eV)	-0.237	-0.64	-0.1486	-0.44
μ	Dipole moment calculates (Deby)	1.577	8.563	0.37	8.781

Table 8

Calculated pharmakinetic parameters of MBH ligand and its metal complexes.

Symbol	Lipinski's rule (limit)	Z- isomer	Cu-MBH	Ni-MBH
Log p (o/w)	Factor of the lipophilicity (< 5)	3.974	2.721	3.974
HBD	Number of hydrogen bond donor sites (≤5)	2	4	3
HBA	Number of hydrogen bond acceptor sites (≤ 10)	4	6	5
mr	Molar refractivity (40-130)	116.33	107.75	116.33
TPSA	Total polar surface area <140	65.1	67.8	67.8
E gap	Energy gap (eV)	-7.33	-8.84	-6.55
% ABS	Absorbance percentage	86.5	85.4	85.6
Log S	Solubility parameter	-3.0668	-2.9525	-3.8598



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

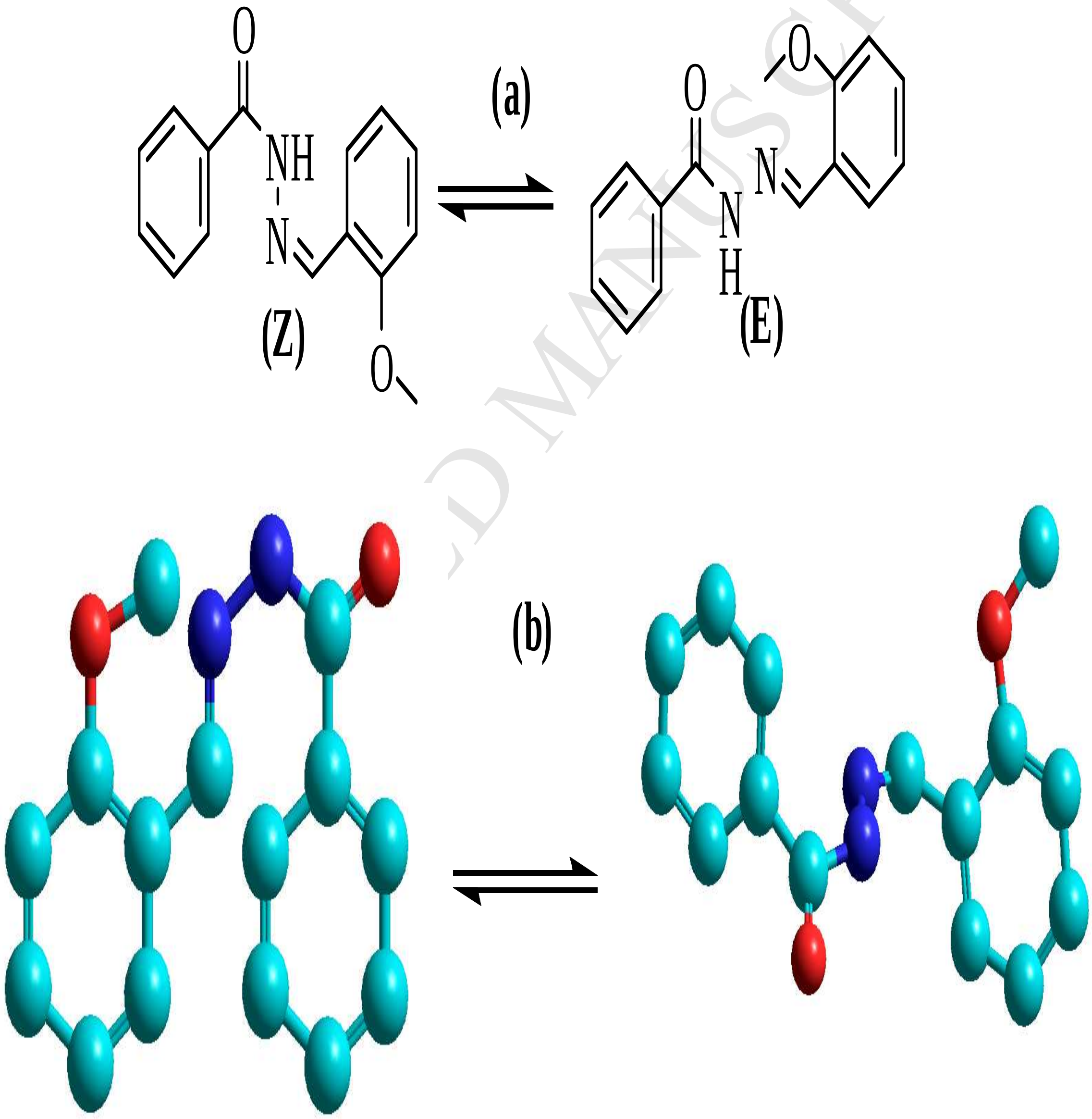


Fig. 1 (a) The chemical structure of Z- and E-forms of MBH ligand.
(b) The minimum energy of MBH ligand, which represented in ball and stick model, carbon in magenta, nitrogen in blue, oxygen in red, the hydrogen atoms removed for clarifying.

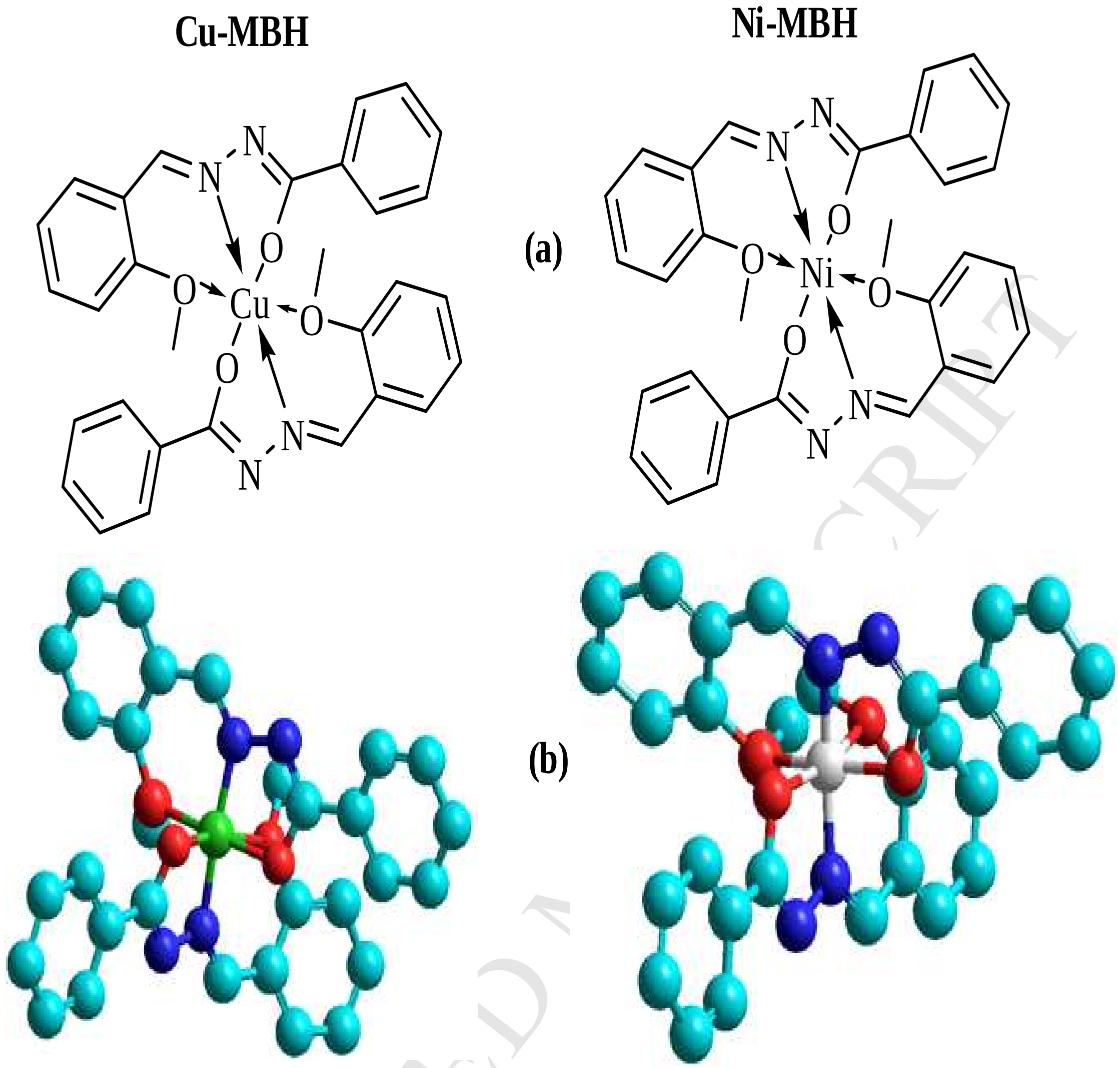


Fig. 2 (a) The chemical structure, coordination cores of MBH metal complexes.
(b) Minimal energy conformation of MBH ligand, represented in ball and stick model, which carbon in magenta, nitrogen in blue, oxygen in red, Cu in green, Ni in white, hydrogen atoms were deleted for clarifying.

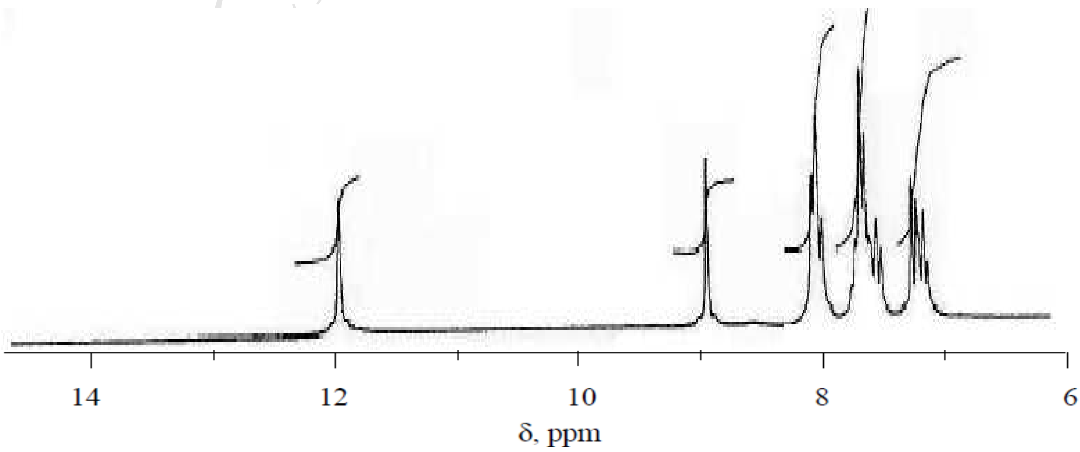


Fig. 3 ^{1}HNMR spectra of o- methoxybenzaldeyhde benzoylhydrazone (MBH) ligand.

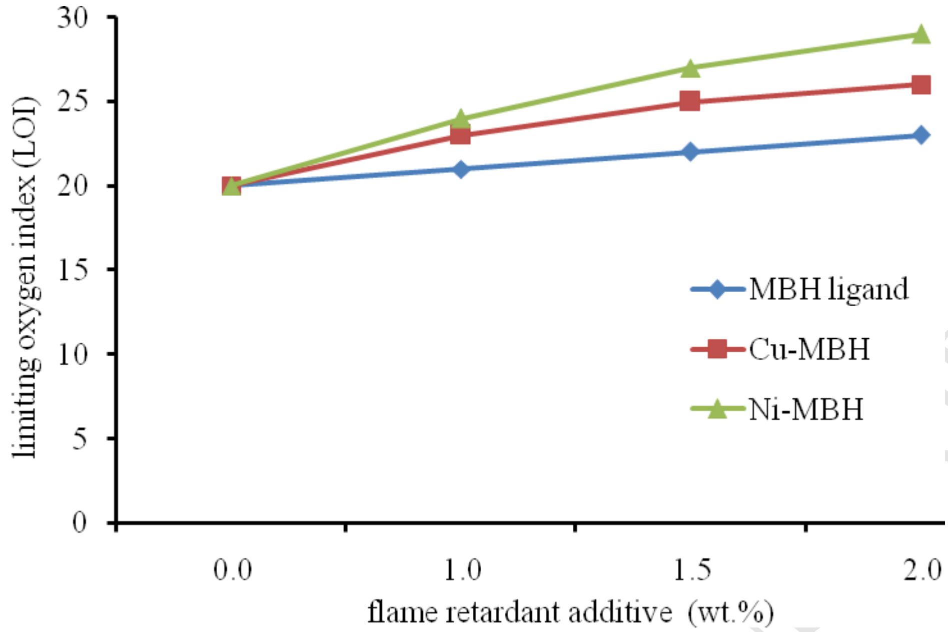


Fig.4 Limiting oxygen index (LOI) characteristics of polyurethane coating incorporated MBH ligand and its metal complexes as flame retardant additives.

Research Highlights

- Hydrazone ligand and its metal complexes have been prepared and characterized.
- The ligand and its metal complexes added physically into polyurethane coating.
- The metal complexes showed better flame retardant activity than the orginal ligand.
- The metal complexes showed better activity than the ligand against the same organism**.**
- Molecular modeling of the free ligand and its metal complexes has been calculated.