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Synthesis and characterisation of sulphonamide (Schiff base) ligand and its copper metal complex and their efficiency in polyurethane varnish as flame retardant and antimicrobial surface coating additives

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Abstract

Sulphonamide compounds are present in many bioactive compounds owing to their multiple biological applications, even their metal complexes. The study reported in this paper focused on the synthesis of a sulphonamide ligand (Schiff base) and its Cu metal complex and their possible applications as anti-microbial and flame retardant additives in polyurethane formulations for surface coating application. Thus, selected divalent (Cu II) metal complex of 4-((E)-(4-hydroxy-3-((E)-(p-tolylimino)methyl) phenyl) diazenyl)-N-(5-methylisoxazol-3-yl) benzenesulphonamide was prepared and characterised using a combination of elemental analysis, Fourier Transform Infrared, Proton Nuclear Magnetic Resonance and mass spectroscopy. The prepared Schiff base ligand and its Cu metal complex were physically added to polyurethane varnish to give varnish coating formulations at a laboratory scale and then applied onto pretreated wood and steel panels using a brush. The oxygen index, Gram negative bacteria; Gram positive bacteria and fungi values obtained indicated that the polyurethane varnish that contained the prepared ligand and its Cu metal complex as additives exhibited very good flame retardant and antimicrobial properties, respectively. It was also found that the metal complex had outperformed the ligand. The physical and mechanical resistance of the coatings was also studied, in order to assess any

disadvantages owing to the incorporation of the additives. It was found that the additives did not influence the flexibility, hardness and adhesion of coating films prepared using the polyurethane varnish. The gloss of the polyurethane varnish film was improved due to the incorporation of the aromatic ring into the formulation.

Keywords: Sulphonamide compounds, Copper metal complex, Fire retardant coating, Antimicrobial coating, Polyurethane coating

1 Introduction

PUs are one of the world's most frequently studied products **[1]**. PUs often shows outstanding and versatile mechanical, chemical and physical characteristics **[2-4]**.

Nitrogen compounds are a small but rapidly growing group of FRs which are in the focus of public interest concerning environment-friendly FRs. Flame-retardant materials based on nitrogen compounds are suitable for recycling, as nitrogen FRs have high decomposition temperatures, their main applications are in melamines for polyurethane flexible foams **[5-7]**. Coumarin derivatives having the thiazole ring incorporated had been studied as eco-friendly antimicrobial, flame retardant and corrosion inhibiting additives for PU coatings. **[8,9]**. Recently, a DOPO-containing imidazole curing agent were synthesized and applied in reactive flame retarded epoxy resin. Also, phosphaphenanthrene, piperidine and triazine-trione groups were simultaneously introduced into the epoxy matrix by chemical linking to obtain a novel intumescent reactive flame-retardant epoxy system. There is review focuses on recent advances in the surface-coating approaches for fabricating flame retarded FPUFs. The design of intumescent and non-intumesecent fire retardant coatings applicable to FR FPUFs are also summarized, finally, some advantages and shortcomings along with future research opportunites are also discussed comparatively **[10-12]**.Hydrazine ligand and its metal

complexes and their potential application as anti-microbial, antifouling and flame retardant additives in epoxy formulations for surface coating application also has been reported **[13]**. Schiff's base compounds had also been added to alkyd paint formulations to render them FR. Limiting oxygen index (LOI) was used to assess the FR properties of these additives **[14]**. The sulphonamides were the first effective chemotherapeutic agents to be employed systematically for the prevention and cure of bacterial infection in human beings **[15]**. Due to that they inhibit the growth and multiplication of bacteria **[16-18]**, sulphonamides ligand and their metal complexes had been screened for antimicrobial activity, the results had shown that the metal complexes had greater activities than their parent ligand **[19-20]**. For the research work reported here, we use a new additive based on new sulphonamide ligand and its copper metal complex, which were blended into chosen polyurethane varnish as additives, with a view to rendering the coating film flame retardant and antimicrobial. Limiting oxygen index (LOI) test was used to assess the flame retardancy properties of the additives. The coatings were tested against gram negative, gram positive bacteria and fungal as antimicrobial additives. The physical and mechanical properties of the coatings were also studied to evaluate any negative impacts that might be caused by the additives.

2 Experimental

2.1 Materials

All of the chemicals used during the study reported here were either obtained locally or from global firms. They were all of high purity and used without further purification. These include salicylaldehyde, a product of Santa Cruz Biotechnology, USA; ethyl acetoacetate, a product of Merck Schuchardt Co. Germany; piperidine, a laboratory product from Merck Millipore, England; thioacetamide (ethanethioamide) and 1-hydroxy-2-naphthaldehyde, a product of

Fluka Chemie AG, Buchs, Switzerland; bromine, a product of Sigma Aldrich Chemical Co. USA; ethyl alcohol absolute, a product of CDH Chemical Co. India; glacial acetic acid and benzene, products of Chemical Co. El-Naser Pharmaceutical, Egypt.

2.2 Methods and techniques

2.2.1 Synthesis of 4-((E)-(4-hydroxy-3-((E)-(p-tolylimino)methyl) phenyl) diazenyl)-N-(5-methylisoxazol-3-l)benzenesulphonamide ligand under microwave irradiation

The equimolar (1:1 ratio) of p-toluidine (0.01mol) with azo-coupled 4-((3-formyl-4-hydroxyphenyl)diazenyl)-N-(5-methylisoxazol 3yl)benzene sulphonamide (0.01 mol) were mixed thoroughly. The reaction mixture was then mixed with 3-4 ml of methanol and irradiated in a microwave oven. The reaction was completed in a 4 minutes at 90w with high yields. The orange colored product was then recrystallised with hot ethanol and finally dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. The progress of the reaction and the purity of the product were monitored by TLC using a silica gel G (yield: 80-90 %). Microwave irradiation was used to induce the desired chemical transformations, in a way that is pollution free, eco-friendly, of low cost and offers high yields together with simplicity in operation and handling **[21]**.

2.2.2 Synthesis of metal complex under microwave irradiation

4-((E)-(4-hydroxy-3-((E)-(p-tolylimino)methyl)phenyl)diazenyl)-N-(5-methylisoxazol -3-yl)benzenesulphonamide and metal salt, $Cu(CH_3COOH)_2 \cdot H_2O$ at (2M:1M) were mixed together. The reaction mixture was mixed with 1-3 ml of ethanol and irradiated with microwave. The reaction completed in a 3-10 min giving higher yields. The resulting product was washed with ethanol and ether and finally dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator **[22]**.

The progress of the reaction and purity of the product was monitored by TLC using a silica gel G (yield: 89 - 93 %). Relevant physical and analytical data of the reactants and products are given in **Table 1**.

Table 1 Physical and analytical data for ligand (HL) and its copper metal complex

[Cu(L_2)2]	**Ligand [HL]**	**Characteristics**		
$C_{48}H_{40}N_{10}O_8S_2Cu$	$C_{24}H_{21}N_5O_4S$	Formula		
(L_2Cu)	HL	Symbol		
>300	260	Melting point (^oC)		
93	94	Yield (%)		
10	4	Time(min)		
Dark Green	Orange	Color		
	7.13-8.33 (t, 1H, phenyl C_6-H_6), 2.32-2.37 (d, 1H, CH_3), 6.18 (s, 1H, oxazole C-H), 14.15 (s, 1H, 1H, OH), 10.38 azomethine C- H), 8.035 (s, (s, 1H, triazole NH)	^{1}H-NMR Chemical shift (δ ppm)		
56.69	60.62	Calc.	C	Elemental analysis (%)
56.94	61.35	Found		
3.98	4.45	Calc.	H	
3.98	4.45	Found		
14.41	14.73	Calc.	N	
13.83	13.49	Found		
6.33	6.74	Calc.	S	
6.24	6.67	Found		
1012	475.5	Calc.	M. Wt.	
	475	Found		

2.3 Preparation of coating compositions and coating films

The coating compositions were prepared by means of incorporating sulphamethoxazole ligand and its copper metal complex in the ratio of 0.5 and 1.0 wt.%, into polyurethane varnish. The composition of the polyurethane varnish is tabulated in **Table 2**. The coating compositions were applied by means of a brush to steel and wood panels. All efforts were made to maintain a uniform film thickness of 50 +/- 5µm.

Table 2 Composition of the studied polyurethane varnish

Component	**wt. %**
Refined sunflower oil	33.42
Glycerol	0.039
Litharge (lead oxide catalyst)	00.03
Pentaerythritol	04.61
Turpentine	47.30
Barium octoate drier	00.26
Toluene diisocyanate	11.37
Mixed drier	02.11
UV absorber	00.26
Anti-skinning agent	00.32
Fire retardant &antimicrobial additives	00.5 to 1.00

Specifications of the PUs formula are: Viscosity: G-I (Gardner); color: 3 (Gardner); solid content: 53 ± 2%.

2.4 characterization techniques

The IR spectra was recorded on a Mac FT-IR spectrometer (KBr technique). The ^{1}H NMR spectra (DMSO-d6) was measured using a Varian Mercury-300 NMR spectrometer at Micro-analytical Centre, University of Cairo. Mass spectroscopy was measured at Al-Azhar University's Regional Centre for Mycology and Biotechnology. Scanning electron microscope

(SEM), the surface morphology of the copper metal complex was observed with the help of a scanning electron microscope (Joel Jsm 6360LA, Japan) at an accelerated voltage of 10 kV. The fracture surfaces were vacuum coated with gold for scanning electron microscope (SEM).

2.5 Antimicrobial screening

2.5.1 Assay medium for antifungal activity (g/l)

The Dox medium was used for antifungal activity. This medium was composed of: Sucrose 20.0; $NaNO_3$ 2.0; K_2HPO_4 1.0; $MgSO_4 \cdot 7H_2O$ 0.5; KCl 0.5; $FeSO_4 \cdot 5H_2O$ 0.001 and agar 20. The pH was adjusted to 6-6.4.

2.5.2 The organism used

Micrococcus lutus NCTC 9341, *Staphylococcus aureus* NCTC 7447, *E. coli Bppol*, and *Salmonella* were the bacteria employed in microbiological testing. The fungi used were *Candida albicans* IMRU 366 g, *Aspergillus flower*, *Peniccilium citricus* and *Suserium*.

2.5.3 Preparation of testing sample

On each side of a Whatman filter paper (No. 30), the varnish to be tested was brushed on and allowed to dry for 24 hours. Coated filter paper squares (1.25 in.) were made. Each of the squares was sterilized by dipping in ethanol. Each of the sterilized squares was centrally placed on agar surface in a sterile petri-dish.

2.5.4 Antimicrobial activity

2.5.4.1 Method for the evaluation of anti-bacteria properties

Twenty four hours culture of each test bacteria and forty eight hours culture of each of the test yeast was used. Five ml of sterile distilled water was added to the culture tube and a vortex mixer has mixed well. To inoculate 100 ml, five drops of suspension were used. Medium of nutrient agar (for test bacteria) or medium of 100 ml yeast extract-malt (for test yeasts) at 45 °C. This was distributed in 20 ml

Petri dishes. Portions A coated filter paper disks (13mm) with the various test organisms were aseptically placed on the surface of the seeded plates. The plates were left for 2 hours in a diffusion refrigerator after which the plates were incubated for the bacteria at 300 °C for 18 hours and yeasts for 48 hours. Detecting clear zone around the paper disc is an indication of the antagonistic properties of the understudy coated filter paper disc and liquid varnishes. At least 4 discs were used for each concentration of sulphonamide ligand and its copper complex for each test organism 0, 0.5, and 1.00 % of the varnish has been investigated

2.5.4.2 The method used for fungi under investigation

After pouring and solidification, the spores and mycelia of each of the test fungi (48 hours old culture) were streaked onto the surface of the Dox medium plates The antimicrobial activity of the coated filter paper disc against a variety of microorganisms, including Gram-Positive, Gram-Negative, Yeasts and fungi was investigated.

2.6 Test method for flame retardants

The efficiency of the blank polyurethane varnish and that of the polyurethane varnish having incorporated ligand and copper metal complex additives were assessed in a limited oxygen index (LOI) chamber following standardized tests ISO 4589-1: 2017 and ASTM D: 2863- 17a. Thus, test panels were prepared using a combustible material (wood specimen). Before the coating application, it was important that the panels were free from any surface contamination or imperfections. Hand tool cleaning (sand paper) was used to thoroughly treat the panel faces and edges. The dry film thickness (DFT) was 60 +/- 5µm. The coating application was implemented through brushing in all instances. The panels under study were heated for two hours at 50-60°C after 10 days of air drying to eliminate

any remaining solvent.

2.7 Physical and mechanical testing of coating films

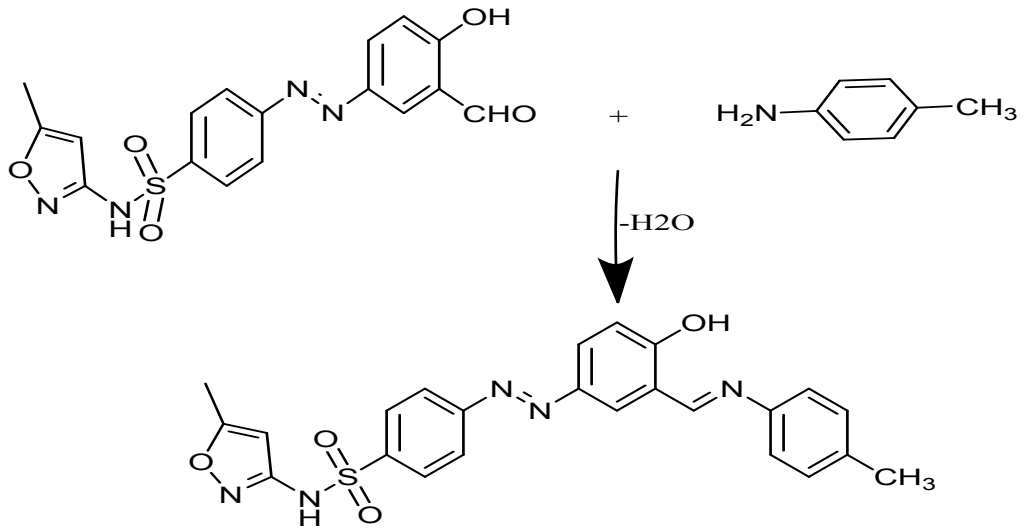
The steel panels were prepared in accordance with ASTM Method D: 609-17. The thickness of the dry film was measured in accordance with ASTM Method D:1005-13. The degree of gloss was measured in accordance with ASTM Method D 523-14. The hardness of the film was measured in accordance with ASTM Method D: 3363-11e. The adhesion was measured in accordance with ASTM Method D: 3359-17 and the flexibility was measured in accordance with ASTM Method D: 522-17.

3 Results and Discussion

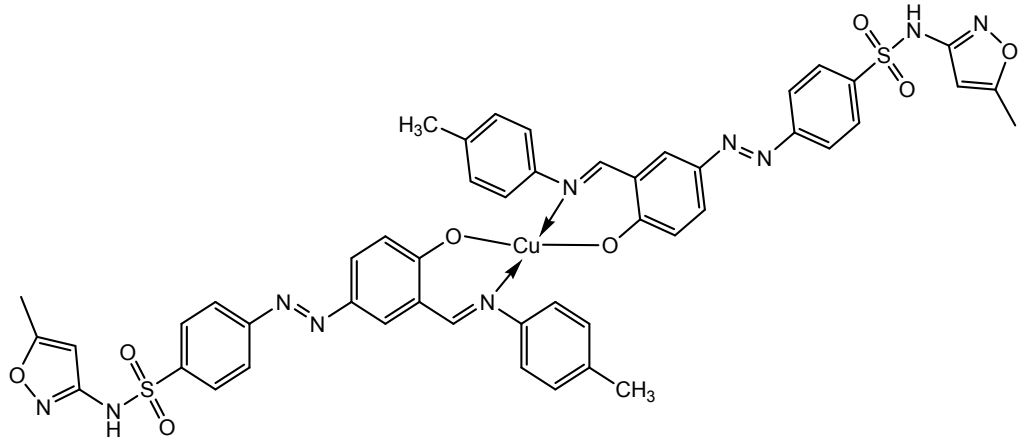
3.1 Synthesis of 4-((E)-(4-hydroxy-3-((E)-(p-tolylimino) methyl) phenyl)diazenyl)-N-(5-methylisoxazol-3-yl) benzenesulphonamide

It was noted as a consequence of microwave aided synthesis that the reaction completed in a shorter time with higher yields than the conventional heating equivalent. In the microwave irradiation method, the homogeneity of the reaction mixture was increased by the rotation of the reaction platform tray. Repeated syntheses confirmed the reproducibility of the outcomes. The newly synthesized Schiff base ligand and its copper metal complex, at room temperature, were colored solid and stable towards air and moisture. The copper complex was insoluble in organic solvents such as ethanol, methanol, DMF, and DMSO. Characteristic peaks in the ligand spectrum and its copper metal complex were regarded and the elemental analysis. FT-IR, compares the composition of the Schiff base ligand. The Schiff base was further used with, Cu^{2+} metal ion using metal acetate for the complexation reaction **[23]**. **Schemes 1** and **2** show the chemical structure of the prepared compounds. Elemental analysis, reaction yield and physical characteristics such as melting point and product color were evaluated

and are listed in **Table 1**.



Scheme 1. The chemical structure of the prepared compound 4-((E)-(4-hydroxy-3-((E)-(p-tolylimino)methyl)phenyl)diazenyl)-N-(5-methylisoxazol-3-yl) benzenesulphonamide ligand



Scheme 2. The chemical structure of the prepared compound copper metal complex of the 4-((E)-(4-hydroxy-3-((E)-(p-tolylimino)methyl)phenyl)diazenyl)-N-(5-methylisoxazol-3-yl)benzenesulphonamide ligand

3.2Spectroscopy studies

3.2.1 FTIR analysis of sulphonamide ligand and its copper metal complex

The prepared ligand's FTIR spectra showed a broad absorbing band at 3432 cm^{-1} that could be assigned to the phenolic -OH group's –OH stretching vibration. The broadening of this band indicates the involvement of the -OH group in hydrogen

bonding **[22]**. The complex's FTIR spectra were compared to the free ligand's spectrum. **Table 3 and Figures 1 and 2** show the most characteristic infrared bands of the free ligand and those of their metal complex. It was observed that, the bands owing to υ (N=N) group which appeared in the spectra of HL at 1470 cm^{-1}. This band shows no significant shift in the metal complex spectrum, **Table 3**, indicating that the N=N group is not involved in complex formation. In the FTIR spectra of ligands, υ (S=O) asymmetric and symmetric vibrations appearing at HL are nearly unaffected in the metal complex. The band that appears at 1284 cm^{-1} in the ligand spectrum corresponds to phenolic groups. The band shifted to a reduced frequency at 1284 cm^{-1} and showed at 1261 cm^{-1} for Cu (II) showing that the metal ion is coordinated after deprotonation through the phenolic group's oxygen atom. The strong band at 1620 cm^{-1} was assigned to the stretching of azomethine ν (C=N) observed in the ligand and this band underwent a shift (~16cm^{-1}) in the complex showing a coordination involvement of the azomethine nitrogen. The new bands observed in the metal complex in the region of (380–355) cm^{-1} and (498–458) cm^{-1} can be attributed respectively to the bands ν (M–N) and ν (M–O) **[24-25]**.

Table 3 Characteristic of IR of the sulphonamide ligand and its copper metal complex

Comp.	N(OH)	N (C=N)	ν (C-O)	ν (N=N)	Nas (S=O)	νs (S=O)	ν (M-O)	ν (M-N)
Ligand	3432	1620	1284	1470	1341	1172		
L_2Cu		1604	1261	1471	1330	1173	498	380

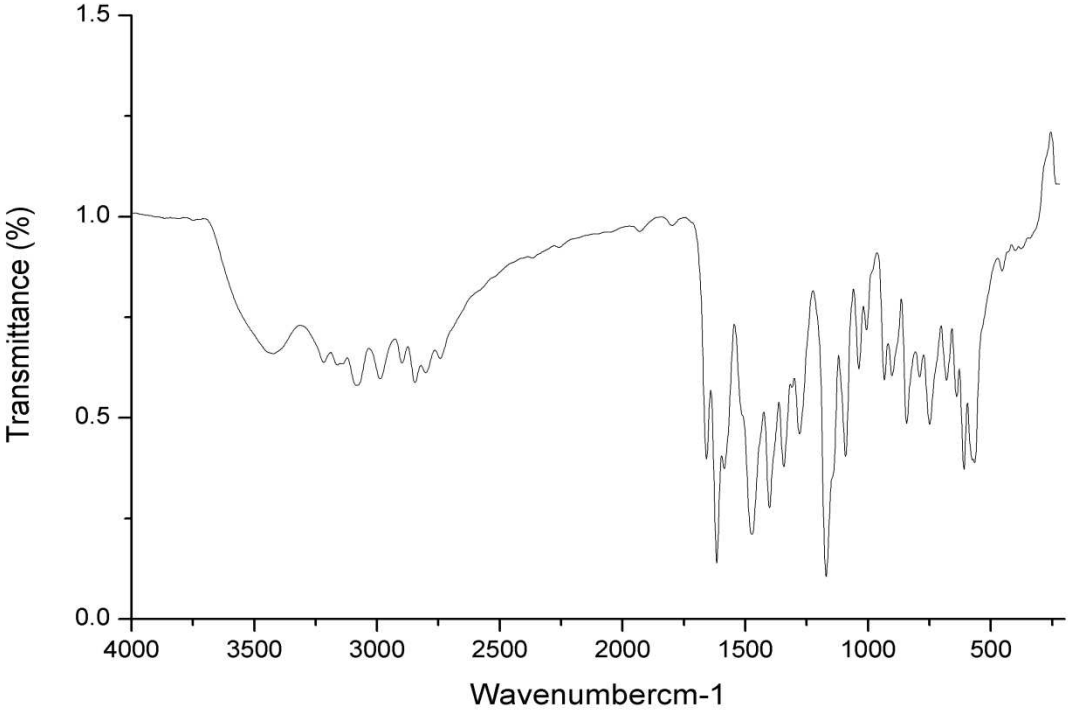


Figure 1 IR spectrum of 4-((E)-(4-hydroxy-3-((E)-(p-tolylimino)methyl) phenyl) diazenyl)-N-(5-methylisoxazol-3-yl) benzenesulphonamide ligand

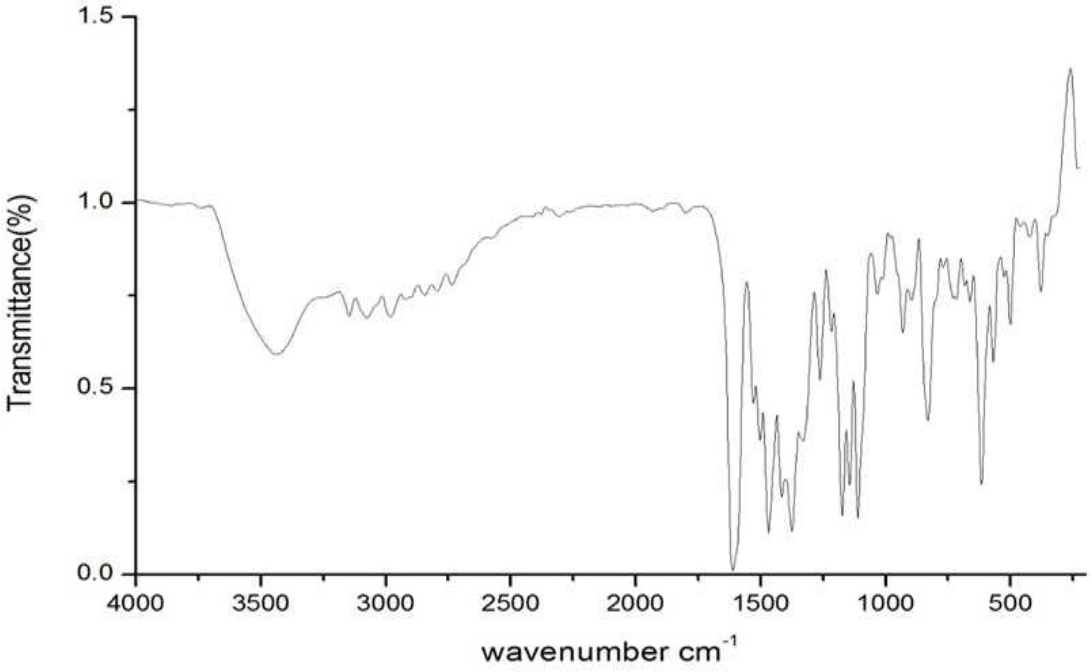


Figure 2 IR spectrum of copper metal complex

3.2.2 ^{1}HNMR of the 4-((E)-(4-hydroxy-3-((E)-(p-tolylimino) methyl) phenyl)diazenyl)-N-(5-methylisoxazol-3-yl)benzenesulphonamide ligand

The proton nuclear magnetic resonance spectra of the ligand, HL, were recorded to allow assignment of the characteristics of the protons to different ligand groups. The sulphonamide ligand ^{1}HNMR spectrum was obtained in d_6-dimethylsulphoxide (d_6-DMSO) solutions using tetramethylsilane (TMS) as internal standard. The interpretation of the ^{1}HNMR spectral data of the ligand **[26]** is as follows: 7.13-8.33 (t, 1H, phenyl C_6-H_6), 2.32-2.37 (d, 1H, CH_3), 6.18 (s, 1H, oxazole C-H), 14.15 (s, 1H, 1H, OH), 10.38 azomethine C- H), 8.035 (s, (s, 1H, triazole NH). The data acquired are shown in **Table 1**.

3.2.3 Mass Spectra of the ligand

The mass spectra of the sulphonamide ligand, were measured to verify their structure. Because the azo compounds have the same molecular formula and formula weight $C_{24}H_{21}N_5O_4S$ M.Wt. 475.5 g/mol), their mass spectra show a molecular ion peak corresponding to the molecular mass of the respective compounds, where, mass spectra of ligand show parent peak at m/z = 475. This molecular ion peak is in good agreement with the empirical formula as indicated from elemental analyses, as shown in **Table 1**.

3.3.1 Thermal Gravimetric Analysis (TGA) of Cu(II) complex

The TGA thermograms confirms the amount of solvent inside and outside the sphere of coordination and provide information about this compound's stability. The thermogravimetric analysis was performed at temperatures ranging from 10 to1000°C for the copper complex. It was found that the Cu (II) complex was stable up to 120°C, no mass loss was observed below 120°C, eliminating the possibility of molecule water outside the sphere of coordination [27].

3.3.2 Morphological characteristics of Cu (II) complex

The SEM microphotography images obtained for Cu metal complex showed that, the Cu metal complex has a rough surface, dense body and had an amorphous structure as shown in **Figure 3**.

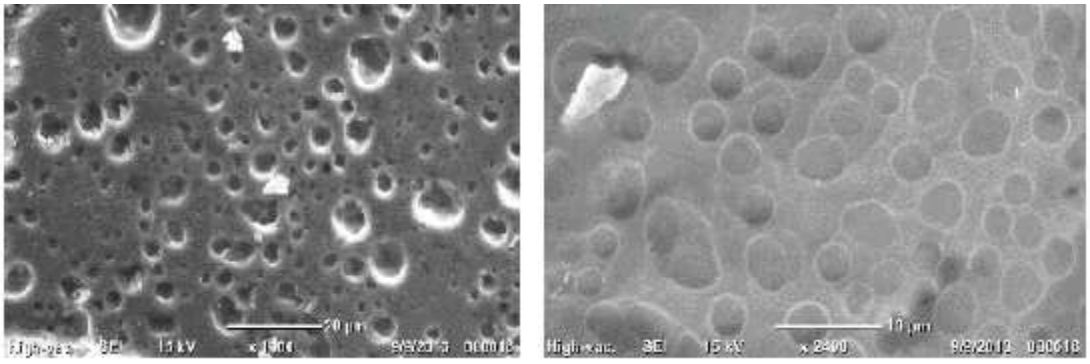


Figure 3. The SEM image of Cu metal complex.

3.4 Characterisation of polyurethane varnish incorporated with sulphonamide ligand and its copper metal complex as antimicrobial and fire retardant additives

3.4.1 Evaluation the antimicrobial activity of the prepared sulphonamide ligand and its copper metal complex as a biocide additive

Biological species can adhere to the surface of a coating under various service conditions that can eventually lead to damage of the coatings. Biocide additives are frequently used to avoid or slow down the growth of bacteria on the coating surface. There are two types of biocides additives used in the manufacture of paint, one is used to protect the wet-state to avoid bacteria and fungi from spoiling the paint during storage, and the other is used to avoid the growth of fungi and algae on the coated surface. The prepared ligand is chemically stable, capable of imparting characteristics of anti-microbial activity when integrated into polyurethane varnish. The anti-microbial activity of the blank and of mixed polyurethane varnish formulations was assessed by subjecting them to Gram-

negative bacteria, Gram-positive bacteria and fungi. Relevant anti-microbial activity results are shown in **Table 4** and **Figure 4** which indicates that the integration of the prepared ligand, by physical means, into polyurethane coating at the levels mentioned in the experimental section, resulted in good anti-microbial activity when compared with the blank polyurethane. This may be due to the biological activity of sulphonamide containing nitrogen and sulphur elements and phenolic hydroxyl in the structure of the sulphonamide ligand. Antimicrobial activity values of polyurethane mixed with copper metal complex are greater than those of the sulphonamide ligand. This may be due to the presence of copper element that enhanced the biological activity of the coating formula prepared. It was also noted that the anti-microbial activity against the target microorganisms rose as the biocide additive concentration rose.

Table 4 Antimicrobial activity of polyurethane varnish having incorporated the prepared ligand and its copper metal complex

Fungi		**Bacteria**				**Additive wt. %**	**Formulation**
		Gram-negative		**Gram-positive**			
G. Candidum	**A. Fumigatus**	**E. Coli**	**P. Aeruginosa**	**B. Subtilis**	**S. Pneumoniae**		
-ve	-ve	-ve	-ve	-ve	-ve	-	**Blank polyurethane**
+ve	+ve	+ve	+ve	+ve	+ve	0.5	**Blank polyurethane &HL**
+++ve	++++ve	++ve	++ve	+++ve	+++ve	1.0	
+++ve	+++ve	++ve	++ve	+++ve	+++ve	0.5	**Blank polyurethane & L2Cu**
++++ve	++++ve	++ve	++ve	+++ve	+++ve	1.0	

Figure 4 The antimicrobial activity of polyurethane varnish incorporated sulphonamide ligand and its Cu II metal complex

The design strategies to control the release of antibacterial agents over space and time can be grouped under three main categories. (A) Passive approaches. By tuning the properties of the coating, it is possible to impose specific preloaded release kinetics, giving the possibility to produce a variety of releases profiles, including rapid bursts (left) or linear release (right) from antibacterial (AB) coatings. (B) Active approaches. External stimuli can be used to trigger the local release of embedded compounds. (C) Bacterial trigger approaches. Bacteria-responsive coatings release antibacterial agents locally when challenged by bacteria, this is represented in **Figure 5 [28]**.

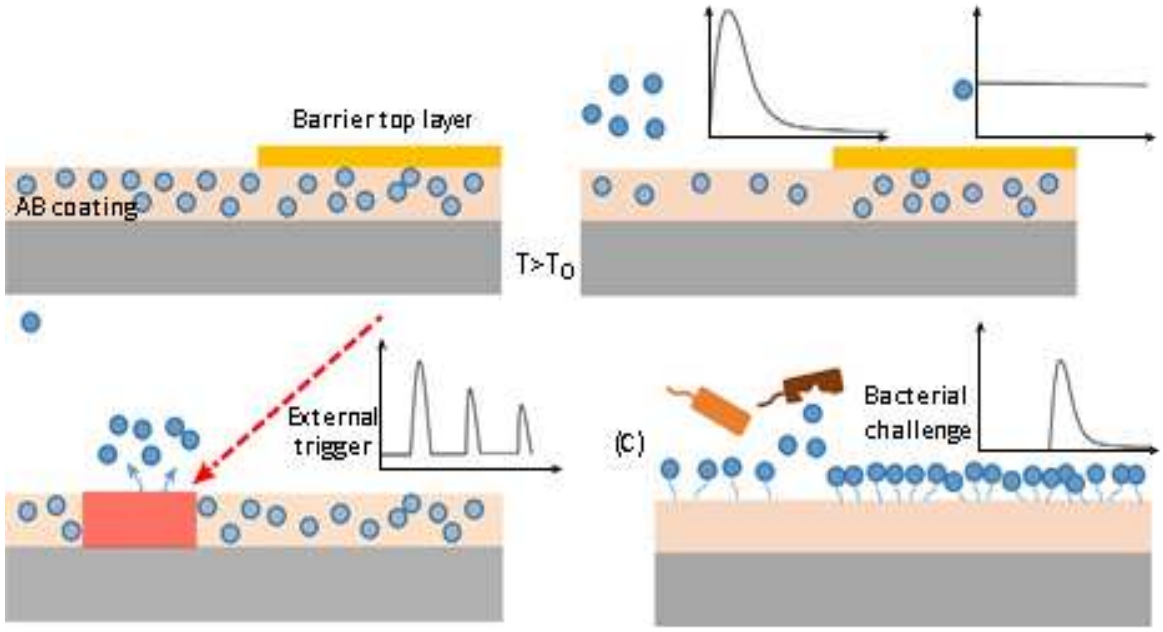


Figure 5 Design of the antibacterial coatings from a 4D view

3.4.2 Evaluation of sulphonamide ligand and its Cu metal complex as flame retardant additives incorporated into a polyurethane varnish

Using the limiting oxygen index (LOI) test, the flame retardant characteristics of the polyurethane varnish mixed with sulphonamide ligand and its Cu II metal complex were assessed; the used LOI chamber is shown in **Figure 6**. The LOI is described as the minimum concentration of oxygen, expressed as a percentage that supports a polymer's combustion. It is assessed by passing over a burning specimen a combination of oxygen and nitrogen and decreasing the amount of oxygen until researching a critical level. An elevated requirement for oxygen concentration shows a greater sample flame retardancy. It was evident from the test results that, when compared with a blank polyurethane sample, the inclusion of sulphonamide ligand and its Cu II metal complex physically added to polyurethane varnish at the ratios shown in Table 5 rendered the coating more flame retardant. **Table 5** shows the outcomes acquired from the LOI test.

Table 5 The flame retardant activity of polyurethane varnish incorporated sulphonamide ligand and its Cu II metal complex

Formulation	**Wt.%**	**Limiting oxygen index (LOI)**
Blank polyurethane	-	20
Blank polyurethane & Prepared Ligand	0.5	38
	1.0	55
Blank polyurethane & Cu metal complex of sulphonamide ligand	0.5	45
	1.0	64

It can be observed, from **Table 5**, that the LOI value of the polyurethane varnish without the additive compound was 20 and that with the additive compound reached 64. Normal atmospheric air contains about 21% oxygen, so a material with less than 21% LOI would readily burn in air. In contrast, a material with a LOI value of higher than 21% but less than 28% would be regarded as "slow

burning". A self-extinguishing material is one that would stop burning after the fire or ignition source has been removed. Clearly, the increase of the contents of sulphonamide ligand and its Cu II metal complex additives increased the LOI value of the polyurethane varnish system. This is due to the integration of the sulphonamide ligand and its Cu II metal complex into the polyurethane thermoset polymer network, which improves polymer's flame retardants, and the flammable synergy of nitrogen, sulphur and copper. This is also due to the fact that they are compounds of high molecular weight comprising nitrogen, sulphur and copper and therefore provide superior flame retardant characteristics compared to low molecular weight flame retardants [29] . Another interesting observation is that the LOI values of the copper metal complex of sulphonamide are the highest. The mechanism that underpin such attractive characteristics (flame retardant) of the coating system is illustrated in **Figure 7 [30]**. The coating system concerned, consists of a base coating layer, a foam layer and a top coating layer. The coating starts foaming when the atmospheric temperature reaches 250 to 300 °C when exposed to fire. To provide superior heat insulation, the foam expands to 25 to 50 times in volume.

Figure 6 Limiting oxygen index (LOI) chamber

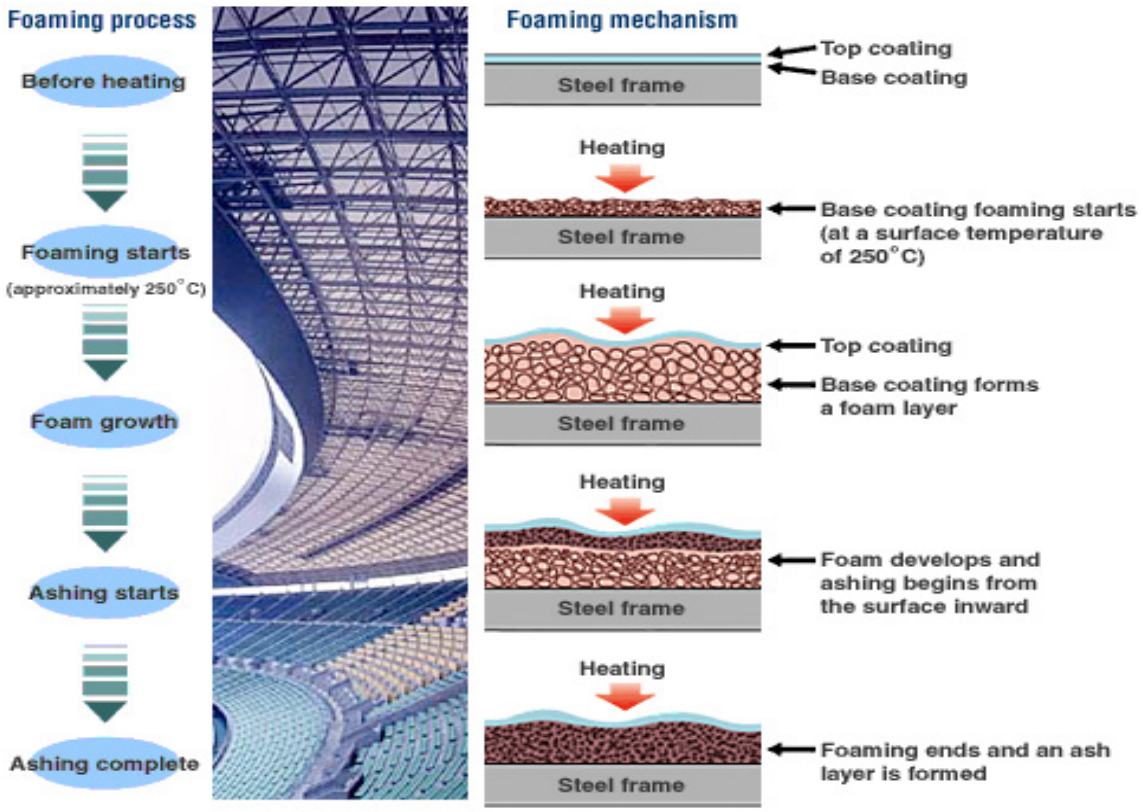


Figure 7 The Mechanism of the attractive properties (flame retardant) of the proposed paints

3.6 Evaluation of the physical and mechanical properties of the polyurethane varnish that incorporated the prepared ligand and its Cu metal complex

The impact of adding the prepared ligand to the polyurethane varnish on the physical and mechanical characteristics of the resulting coating was assessed as per standard test methods. This was performed to determine whether any adverse effect might have resulted from the addition of the additives. In particular, properties including gloss, scratch hardness, cross hatch adhesion and flexibility were evaluated. Relevant results are shown in **Table 6**.

Table 6. Physical and mechanical characteristics of polyurethane coating that incorporated prepared ligand and its Cu metal complex

Formulation	%	Gloss at 60 °C	Hardness(Kg)	Adhesion	Flexibility
Blank polyurethane	-	80	<2	5B	Pass

Polyurethane & Ligand	0.5	82	>2	5B	Pass
	1.0	84	>2	5B	Pass
Polyurethane & LCu complex	0.5	86	>2	5B	Pass
	1.0	86	>2	5B	Pass

3.6.1 Gloss

Gloss was evaluated using a gloss meter supplied by Sheen UK. When observing the coating films at an angle of 60°, it could be seen that the prepared ligand and its Cu complex additives effectively improved the PU's gloss levels. This is obviously a positive result that can be ascribed to the additive structure which (prepared ligand and the Cu complexes) contain many aromatic rings in its chemical structure and which improving the Gloss value of the coated films and also the metal complexes had been found can be improve the value of this test [13, 14].

3.6.2 Scratch hardness

This was determined by using a Sheen, UK scratch hardness tester. The scratch hardness was observed to be >2Kg and it was evident from the data that as the content of the prepared ligand additive increased, the coating film's scratch hardness increased compared to the coating film without the additive (blank sample). Such an improvement in film hardness may be due to the structural reinforcement resulting from the presence of the sulphonamide ligand and its Cu metal complex.

3.6.3 Cross-hatch adhesion

Cross-hatch adhesion test was conducted using a Sheen, UK crosscut adhesion tester. Thus, on the coating film, a lattice with six cuts in each direction (the cuts were spaced at 1 mm) was made for this test method. Then, pressure-sensitive tape was applied over the lattice and peeled off. It was found that all of the coating

films showed good cross-hatch adhesion. As such, it was concluded that the prepared ligand additive and its copper metal complex did not negatively affect the adhesion characteristics of the polyurethane varnish system.

3.6.4 Flexibility (bending)

A ¼ inch Mandrel bends tester supplied by Sheen, UK was used to conduct the flexibility (bend) test. The panel surface was positioned to face outward. The coating films of all of the compositions mentioned above passed the ¼ inch Mandrel bend test. The varnish was deemed to have satisfactory flexibility if after the bending operation no crack mark or dislodging was noted. It was found that all of the coating films showed fairly good flexibility based on experimental results.

4. Conclusions

In the research study reported here, a Schiff base, sulphonamide ligand (HL), namely 4-((E)-(4-hydroxy-3-((E)-(p-tolylimino)methyl)phenyl)diazenyl) -N- (5-methylisoxazol-3-yl)benzenesulphonamide and its copper complex were synthesised and characterised. The SEM confirmed that, the Cu metal complex has a rough surface, dense body and had an amorphous structure. The ligand and its copper metal complex have been physically incorporated into a polyurethane coating to study their antimicrobial and flame retardant properties. The study showed that the activity order of the synthesised ligand and its metal complex against microorganism can be represented as LCu > sulphonamide ligand. Further, it was found that in general, under the same experimental conditions, the metal complex showed higher activity than the free ligand against the same organism. The flame retardant activity order can be represented as LCu > sulphonamide ligand. Such an enhancement is likely due to the introduction of; nitrogenous compounds of high molecular weight; the aromatic ring; and high melting point metals. The findings made also showed that the antimicrobial activity against the

target microorganisms and the flame retardant characteristics improved with the increase in the level of addition of the metal complex. It was also found that with a rise in the ligand and the metal complex content within polyurethane, the mechanical characteristics of the coating film improved. Due to its simple synthesis, highly potent antibacterial, antifouling and flame retardancy at low concentration, the new materials reported here may provide a promising approach to a diverse range of applications.

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

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