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RESEARCH ARTICLE

HYDRAZONE COMPOUNDS OBTAINED FROM 5-NITROSALICYLALDEHYDEBENZOYL HYDRAZONE_BASED LIGANDS AND THEIR COMPLEXES Fe^{2+} and Mn^{2+} and: SYNTHESIS, CHARACTERIZATION, AND ANTIMICROBIAL ACTIVITIES

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ABSTRACT

By reacting an alcoholic medium of 5-nitrosalicylaldehyde with Benzhydrazide to create the complementary Schiff base HL^{+}, a hydrazone Schiff base has been created. FT-IR spectral distinction, magnetic susceptibility, and UV-Vis spectroscopy were utilized to determine the melting temperatures of the synthesize compound Fe(II) and Mn(II). At room temperature, the resultant Schiff bases and complexes are lively and stable. The composite were seen to be mixable in organic solvents such Dimethyl Sulphoxide, acetone, and ethyl alcohol and imixible in pure water. These metal ions have been given an octahedral shape based on magnetic and spectroscopic observations. The synthesis of azomethine was shown by the band at 1580 cm^{-1} in the Schiff base's spectral data. The nitrogen atom of the imino compound group is coupled with the metallic material ions, and as a result, complexation occurs at the Nirogen-atom of the azomethine group. This is evidenced by the band's migration to a higher wavenumber in the complexes. By comparing the metal(II) complexes and Schiff base to four bacterial strains S. aureus (Gram positive), P. aeruginosa, K. pneumonicae, E. cloacae (Gram negative), and two fungi species A. niger and P. Infestans antibacterial and antifungal properties were determined. The composite showed greater antimicrobial properties as opposed to the ligand in its free form, according to the results of comparing the hindrance levels of the azomethine and its composites.

KEYWORDS

Schiff bases, 5-nitrosalicylaldehyde, Benzhydrazide Antimicrobial activity, Synthesis

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Introduction

Therapeutic Non-organic chemistry, a prominent research area focused on the use of metallic based_compounds for disease treatment and diagnosis (Orvig and Mjos, 2014), has been significant in this context. Despite the historical use of metallic_based remedies dating back to pre_history era, therapeutic non-organic chemistry is relatively new compared to other fields of medicinal chemistry, such as biotherapeutic drugs and small organic molecules. For example, the Greek physician Hippocrates used silver to remedy injuries and ulcers, while gold was employed for remeding diseases in olden days China (Wuana et al., 2020).

The The study of aroylhydrazones_derivatives involves examining their chemical properties and reactions of related composites has received a lot of curiosity (Liu and Xue, 2006). There are substances that have biological action (Chen et al., 200) and may be used as prospective coordinating compounds (Sivakumar *et al.,* 1996). Many different pharmacological effects are displayed by hydrazones, including analgesic (Alexandre-Moreira et al., 2011), anti-inflammatory (Turan-Zitouni *et al.,* 2010), antibacterial (Palanivelu *et al.,* 2011), (Novellino *et al.,* 2004) antimicrobes, anti-HIV (Travagli *et al.,* 2004), and anticancer. Hydrazones are also among the frequently utilized complexing agents due to their propensity to easily produce a variety of elemens. In transitionalan effort to enhance their therapeutic properties while reducing their toxicity, numerous investigators have developed a number of modified byproducts as pharmaceuticals potential (Lovejoy and Richardson 2002).

Materials and Method

The Analar grade reagents and diluents was procured from Merck KGaA. They were used exactly as they were delivered, without further purification. All weighing was done using a Toledo B154 electric meter weighing balance. Happ Genzel was used to record infrared spectral studies in the 4000-400cm-1 wavelength region. Using a CARY-50 Bio UV-visible spectrophotometer, 300–1000 nm UV-visible spectra of DMF solutions were captured.

Balance of magnetic susceptibility. The complexes' magnetic susceptibility was evaluated using Sherwood MK1. Gallenkamp melting point equipment were utilized to calculate the melting points of the Schiff base and the complexes. Studies on antimicrobial activity were undertaken in the department of Microbiology University of Dutsin-Ma, Katsina's Microbiology Department. In the same department, isolates of the positive Staining bacteria Staphy aureu and negative Staining K. pneumonicae, Pseudomonas aeruginosa, and Enterobacter cloacae, as well as the fungi Aspergillus niger and Phytopthera Infestans, were recovered and identified.

Synthesis of the Schiff base ligand

Benzoylhydrazide (0.6808g) and 5-Nitro-2-hydroxybenzaldehyde (0.6808g) and combined in an equimolar blend and then heated to a boiling point with condensation in 20cm3 of ethanol for 24 hours. Following that, the solution was sieved to get rid of certain undissolved solids. After 6 days of room temperature evaporation, the filtrate contained colorless crystals (Fig. 1).

Synthesis of the Schiff base complexes

The metallic salts (e.g., 0.096g of CrCI3.6H2O, 0.0959gl) and the ligand (0.1g) were combined in 20 $cm^3$of ethanobiologicall. After that, the composites is then heated to a boiling point with condensation in a time of four hours. The Composites is enabled to solidify in room temperature, for several days. Solid that formed was seperated from the liquid usinga filter, then cleaned in 2cm^3 ethanol and 5cm^3 ethyl ether, allowed to dry. The remaining composites saw similar outcomes (Demet et al., 2014). The salts $CuSO_4.5H_2O$, $Co(NO_3)_2$, and $NiCl_2.6H_2O$ were used to make the complexes.

Antimicrobial study of the coordinating compounds and their transition metal complexes

The activities of synthesized 5nSBH and their metallic compounds were examined for bactericidal and fungicidal properties employing disc method on Mueller Hinton agar (MHA) and Sabourad dextrose agar (SDA) sterile plates. To identify the minimum concentration needs to inhibit microbial growths (MCI) values (μg/ml

), then a stock solution is made by dissolving the compounds to a specific concentrations of 200 × 10^3 μg/ml 40 ×10^3 μg/ml, and 8 × 103 μg/ml in DMSO.Four bacterial strains, including the S. aureus (gram positive) as well as K. pneumonicae, Pseudomonas aeruginosa, then finally Enterobacter cloacae (gram_ negative), incubation was carries out at 37°C for a period of 24 and 48hrs, (Yusha'u, 2011).

Fluconazole, an antifungal medication, and Ciprofloxacin, an antibiotic, were employed to evaluate the efficacy of the synthetic alternatives. The antibacterial and antifungal effects of the common antibiotic Ciprofloxacin and the antifungal medication fluconazole were also evaluated at the same concentration and under circumstances that were similar to the concentration of the test compounds. Antimicrobial activity studies were carried out in triplicate, with the average being the final outcome. The diameter of the antibacterial activity inhibition zones surrounding the disc was assessed (NCCLS, 2008). The studies were completed at the University of Dutsin-Ma in Katsina state microbiological lab

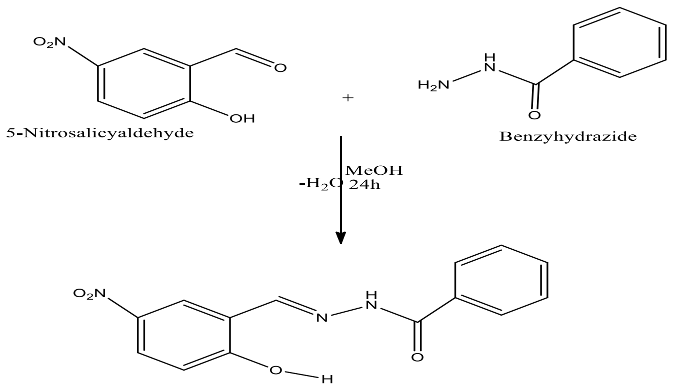

figure 1: 5-Nitro-2-hydroxybenzaldehyde benzoylhydrazone

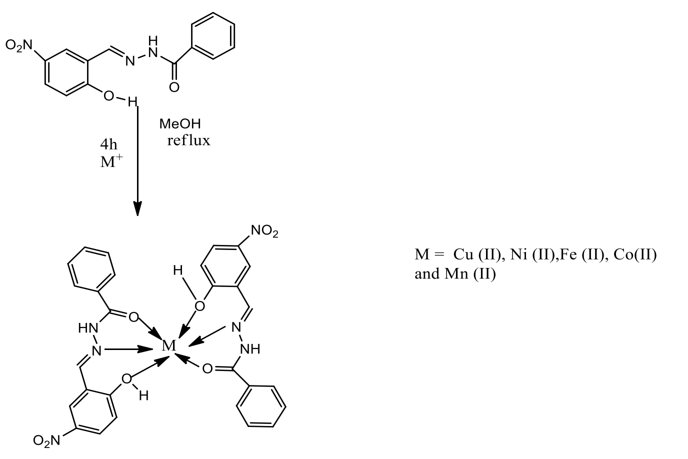

figure 2: Suggested structure of metallic (II) complex

Results and Discussion

Figure 1 shows that a 1:1 mole ratio of 5-nitro-2-hydroxybenzalldehyde and bezyhydrazide was used to condense the Schiff base. According to Table 1, the reaction between the ligand and metal (II) salts (figure 2) led to the formation of compounds with a large yield and distinct colors. The spin magnetic moment for the Fe(II) and Mn(II) Suggested paramagnetic behavior and high spin complex due to the numbers of unpaired electrons.

Table 1: Physical Characteristics of the Ligand (HL) and their Metallic (II) Complexes

Compound	Molecular formula	Mol wt (g/mol) μeff	Colour	Percentage Yield (%)	Melting Temp (⁰C)
HL	$C_{14}H_{11}N_3O_4$	285.1	Yellow	59	130
[Fe (HL)$_2$]	[$FeCl_2.6H_2O$ ($C_{14}H_{10}N_3O_4)_2$]	769.0 4.31	Green	74	215
[Mn (HL)$_2$]	[$Mn(NO_3)_2$ ($C_{14}H_{10}N_3O_4)_2$]	768.0 4.05	Pink	74	136

Key: HL – 5-nitro-2-hydroxybenzaldehyde benzoylhydrazone

Table 2: Dissolvability data of the Ligand (HL) and their metallic (II) complexes

Solvent Compound	DistH_2O	MeOH	EtOH	Chloroform	Benzene	DMSO	Hexane	Acetone
HL	IS	S	S	S	SS	S	S	S
[Fe(HL)$_2$]	IS	SS	S	SS	SS	SS	SS	S
[Mn(HL)$_2$]	IS	S	S	S	S	S	S	S

Key: **S- soluble, IS - insoluble, SS – sparingly soluble, HL- 5-nitro-2-hydroxybenzaldehyde benzoyl hydrazones**

IR spectral Studies

The schiff base IR spectum shows medium to strong intensity absorption bands at 1677 and 1580 per centimeters are were ascribed to the elongating modes of the carbonyl group (CO) and imine (CN). The FT-IR spectrum value for the chelator and the compounds is provided in Table 3. The IR spectrum complexes and that of the unbounded chelator were contrasted in order to determine the participation of binding sites in the compounds.

The spectral of the unbounded schiff base 5nSBH showed different absorption peaks at 1282 and 3063 cm^{-1}, which are brought on by v{N-N} and v{N-H}. The complexes dramatically change the strong peak at 1580 cm^{-1} v{C=}) in the spectrum.

This peak went to the higher wavenumber in the complexes. This shows that the imine N(Niyrogen) is linked to the metallic ions, and as a result, complexation takes place through the N-atom of the azomethine group, in accordance with (Koley *et al.,* 1989). In the spectra of metal nitrate and chloride complexes, the v{NH} peak remains essentially unaltered or shifted to higher frequencies, suggesting that this group is not involved in coordination and that there may be a decrease in hydrogen bonding during binding sites.

In light of this, the significant shifts of the v{OH} group peak at 3063 per centimeter in the spectrum of the ligand, shifted towards higher frequency side in the compounds which is also an indication of the involvement of v{OH} in bond formation in the complexes demonstrated that phenolic oxygen is binded to the metal. In a similar vain it also indicate the participation

Table 3: Diagnostic FT-IR band (cm^{-1}) in HL and its metal complexes

Compound	v(C=O)	v(C=N)	v(NH)	v(OH)	v(N-N)
HL	1677	1580	3063	3063	1073,1282
[Fe $(HL)_2$]	-	1602	3369	3220	1073,1282
[Mn $(HL)_2$]	1677	1595	3436	3436	1282,1073

Antimicrobial activity

Using the disc diffusion method, the antibacterial activity of the Schiff base and its metal (II) complexes were assessed. For each treatment, the diameters of the inhibitory zone (mm) were assessed. At the same concentration and in the same environment as the test compounds, the antifungal drugs fluconazole and the reference drug ciprofloxacin were tested for their antifungal and antibacterial efficacy. The negative control was a disc of DMSO that had been poured. The antibacterial efficacy of the produced ligands and their complexes against S. aureus, Pseudomonas aeruginosa, K. pneumonicae, and Enterobacter cloacae was evaluated (Table 4.0). Results of the bactericidal activity of the Schiff base ligand against all the tested species revealed little to no action. S. aureus, Enterobacter cloacae, and Pseudomonas aeruginosa bacterial strains have been reported to be resistant to the Fe(II) metal complex, but K.pneumonicae is more vulnerable to attack. S. aureus, however, exhibits notable excellent activity against the Mn(II) complex but is insensitive to Enterobacter cloacae. When compared to ligands and its metal (II) complexes at the same concentrations, the conventional medication Ciprofloxacin shown good effectiveness against all pathologens species with a higher zones of inhibition.

Table 4: Bactericidal activity of schiff base HL and their metallic (II) complexes

Test organisms	Compounds	Zones of inhibition (mm)
Staphylococcus aureus	HL [Fe $(HL)_2$] [Mn $(HL)_2$] Ciprofloxacin	- - 14.0±4.35 36.0 ±0.577
Pseudomonas aeruginosa	HL [Fe $(HL)_2$] [Mn $(HL)_2$] Ciprofloxacin	5.0 ±2.645 - 11.0±2.88 46.0 ±2.081
Enterobacter Cloacae	HL [Fe $(HL)_2$] [Mn $(HL)_2$] Ciprofloxacin	- - - 39 ±2.640
Klebsiella pneumonicae	HL [Fe $(HL)_2$] [Mn $(HL)_2$ Ciprofloxacin	- 6.0± 2.081 12.0±1.154 13.0 ±3.210 35.0 ±0.577

The Schiff base and its complexes were tested for antifungal activity, and the findings are shown in Table 5. The ligands had good antifungal efficacy against the two tested fungal isolates, according to the antifungal activity results. The complexes did, however, exhibit noticeably effective activity against the fungi Phytopthera Infestans and Aspergillus niger. The Phytopthera Infestans strain had good effectiveness against Aspergillus niger but was resistant to the fluconazole-based medications.

Table 5: fungicidal activity of Schiff base HL and their metallic (II) complexes

Test organisms	Compounds	Zones of inhibition (mm)
Aspergillus niger	HL [Fe (HL)$_2$] [Mn (HL)$_2$] fluconazole	35 ±0.577 8±0.577 11±0.577 35.0 ±3.78
Phytopthera Infestans	HL [Fe (HL)$_2$] [Mn (HL)$_2$] fluconazole	35.0 ±2.081 21.0±2.516 32.0±3.210 20.0 ±2.081

Key: H L – 5-nitro-2-bydroxybenzaldehde benzoylhydrazone

Conclusions

Successfully synthesized and described are the hydrazone Schiff base 5-nitrosalicylaldehyde benzoylhydrazone (5nSBH) and their metal (II) complexes of Fe(II) and Mn(II). based on research in electronics and spectrum, magnetic susceptibility, Solubility and determination of their antimicrobial characteristics. For all the synthesized complexes, the structure depicted in figure 1 is the suggested. According to the Infra-red spectral data of the ligand when compared to those of their corresponding metal(II) complexes, the coordination of the metal ion to the ligand is carried out by imiine nitrogen and phenolic (OH) of the hydrazone Schiff base. The magnetic succesptibility of the two complexes indicated that they both have paramagnetic properties and also shows a high spin due to the numbers of unpaired electrons. The metallic (II) complexes that were created had notable bactericidal and fungicidal property, with the compound outperforming the unbounded ligand against different species of pathogens and moulds.

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