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Nickel (II), cobalt (II) and lead (II) complexes of 4-hydroxy-3-methoxybenzaldehyde thiosemicarbazone synthesis; Characterization and antimicrobial activity

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Abstract
This study was carried out for synthesis and characterization of 4-Hydroxy-3-methoxybenzaldehyde thiosimcarbazone and its Nickel (II), Cobalt (II) and Lead (II) complexes and to evaluate their antimicrobial activity. The synthesized compounds were characterized by FT-IR and UV-Vis. The results of FT-IR and UV-Vis spectra of the ligand and its metal complexes confirm the formation of azomethine group (-C=N-NH) accompanied with the absence of carbonyl group (C=O) and the formation of (M-N) and (M-S) bonds with all metal complexes. The results assign that the ligand is neutral and bidentate species witch coordinated via azomethine N and thione S with all three metal ions. The antimicrobial activity of the ligand and its metal complexes was carried out against four types of bacteria (*Bacillus subtilis, Pseudomonas aeruginosa, and Escherichia coli)* and one fungus *(Candida ablicans)* by using disc diffusion method. The results showed that the ligand was inactive against one fungi (*Candida ablicans)* and three type of bacteria (*Escherichia coli, Pseudomonas aeruginosa* and *Bacillus subtilis*) and partially active against one type of bacteria (*Staphylococcus aureus*), Ni (II) complex was inactive against all tested bacteria and partially active against one fungi (*Candida ablicans)*, Co (II) complex was active against one type of bacteria (*Escherichia coli*) and one fungi (*Candida ablicans)* and partially active against three type of bacteria (*Bacillus subtilis, Staphylococcus aureus, Pseudomonas aeruginosa*), Pb (II) complex was active against one type of bacteria (*Bacillus subtilis*), partially active against three type of bacteria (*Staphylococcus aureus, Escherichia coli* and *Pseudomonas aeruginosa*) and one fungi. The study recommends further work should be done to test these compounds against other types of bacteria and fungi.

Keywords: Vanillin schiff base, metal complexes, antimicrobial activities

Introduction

Coordination compounds have been a challenge to inorganic chemist since they were identified in 19th century. They defy the usual rules of valence at that time and hence called complexes. They play vital role in our lives. Transitions metal complexes with soft or hard donor groups have been used extensively in coordination and organometallic chemistry. Schiff bases are condensation products of primary amines with carbonyl compounds and they were first reported by Hugo Schiff [1] in 1864.

These compounds are also known as anils, imines or azomethines. Several studies [2, 3] showed that the presence of a lone pair of electrons in sp^2 hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are generally excellent chelating agents, especially when a functional group like –OH or –SH is present close to the azomethine group so as to form a five or six membered ring with the metal ion. Versatility of Schiff base ligands and its biological, analytical and industrial applications of their complexes make further investigations in this area highly desirable [4].

Schiff bases are crystalline or oily substances that are insoluble in water and soluble in organic solvents. They are weak bases, forming salts with acids in an anhydrous medium; in aqueous acid solvents, they undergo hydrolysis to yield an amine and aldehyde. The majority of Schiff bases are stable in alkaline solutions. Schiff bases derived from an amino and carbonyl compound are an important class of ligands that coordinate to metal ions via azomethine nitrogen [5].

Thiosemicarbazones are a class of compounds obtained by condensation of thiosemicarbazide with suitable aldehydes or ketones. In most complexes thiosemicarbazones behave as bidentate ligands because they can bond to metals through sulphur and the hydrazinic nitrogen atoms, although in a few cases they behave as unidentate ligands and bond through only sulphur atom.

Thiosemicarbazone derivatives are of special importance because of their versatile biological and pharmacological activities. Thiosemicarbazone derivatives have found application in drug development for the treatment of central nervous system disorders, bacterial infection, as well as analgesic and antiallergic agent. Thiosemicarbazones are potent intermediates for the synthesis of pharmaceutical and bioactive materials and thus, they are used extensively in the field of medicinal chemistry. Moreover, thiosemicarbazones have found their way into almost every branch of chemistry; commercially they are used as dyes, photographic films, plastic and in textile industry.

Materials and methods

Materials

Chemical and solvents

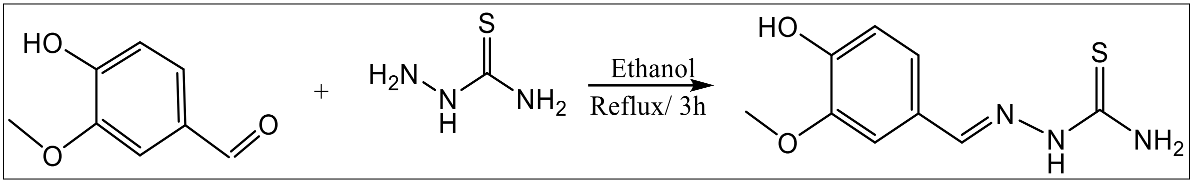
Ethanol, Distilled water, Vanillin (4-Hydroxy-3-methoxybenzaldehyde), Nickel (II) Chloride Hydrate, Cobalt (II) Chloride Hydrate, Lead (II) acetate and Thiosemicarbazide.

Tools and Equipments

Magnetic Stirrer, Reflux condenser, Sensitive balance, Petri dishes, Filter paper, Beakers, Funnel, Incubator, Micropipette, Test tube, FT-IR spectrometer and UV-Vis spectrometer.

Methods

Synthesis of Ligand: Vanillin (4-Hydroxy-3-methoxybenzaldehyde) thiosemicarbazone was prepared by refluxing Thiosemicarbazide with vanillin in (1:1 ratio) for 3 hrs. Thiosemicarbazide (0.91g, 0.01m) in hot ethanol (50ml) and vanillin (1.52g, 0.01m) in hot ethanol (50ml) were mixed the reaction mixture was refluxed for 3 hrs. The condensation product was filtered, recrystallized form ethanol and dried. The yield was 64%.



Scheme 1: Synthesis of 4-Hydroxy-3-methoxybenzaldehyde thiosemicarbazone.

Synthesis of Nickel complex:

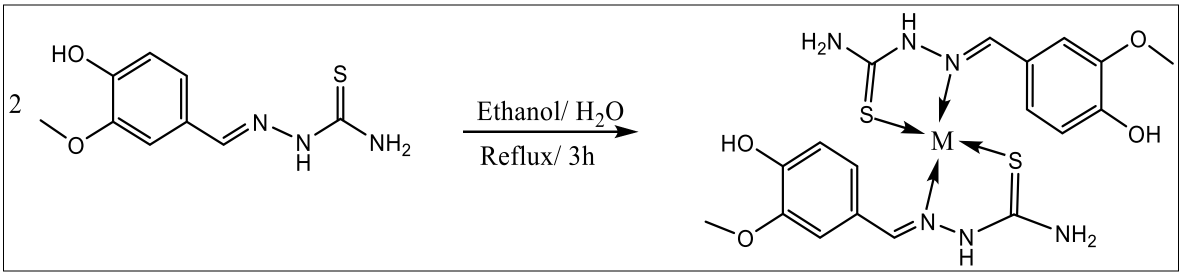
The Ni (II) complex was prepared by addition of hot aqueous solution of the metal chloride (0.2377g, 0.001mmol,) dropwise, to a refluxing ethanolic solution of the ligand (0.4505g, 0.002mmol,) until the metal:ligand ratio reached 1:2**.** The reaction mixture was maintained at the refluxing temperature for 3 hrs. The solid separated was filtered out, washed with ethanol and dried**.** The yield was 63.88%.

Synthesis of Cobalt complex

The Co (II) complex of was prepared by addition of hot aqueous solution of the metal chloride (0.2379g, 0.001mmol,) dropwise, to a refluxing ethanolic solution of The ligand (0.4505g, 0.002mmol,) until the metal:ligand ratio reached 1:2**.** The reaction mixture was maintained at the refluxing temperature for 3 hrs. The solid separated was filtered out, washed with ethanol and dried. The yield was 51%

Synthesis of Lead complex

The Pb (II) complex was prepared by addition of hot aqueous solution of the metal acetate (0.2793g, 0.001mmol,) dropwise, to a refluxing ethanolic solution of the ligand (0.4505g, 0.002mmol,) until the metal-to-ligand ratio reached 1:2**.** The reaction mixture was maintained at the refluxing temperature for 3 hr. The solid separated was filtered out, washed with ethanol and dried. The yield was 71.30%.



Scheme 2: Synthesis of Ni (II), Co (II) and PB (II) complexes of 4-Hydroxy-3-methoxybenzaldehyde thiosemicarbazone.

Chemical Analysis

FT-IR Analysis

The sample was mixed with potassium bromide and pressed under high pressure. The KBr melts and seals the sample into a matrix; the resulted is KBr pellet that can be inserted into a holder in Perkin-Elmer FT-IR type -1650 spectrophotometer in wave number region 4000-200 cm^{-1}.

UV Analysis Assay

0.01g of sample dissolved in 5ml of ethanol, serial dilution many times was made then 1ml of solution placed into sample cell of UV spectrometer-1800-Shimadzu-Japan.

Disc diffusion method (Testing of antibacterial susceptibility)

Paper disc diffusion method was used to screen the antibacterial activity of the prepared compounds was performed by using Mueller Hinton agar (MHA). The experiment was carried out according to the National Committee for Clinical Laboratory Standards Guidelines (NCCLS, 1999). Bacterial suspension was diluted with sterile physiological solution to 10^8cfu/ ml (turbidity = McFarland standard 0.5). One hundred microliters of bacterial suspension were swabbed uniformly on surface of MHA and the inoculums was allowed to dry for 5 minutes. Sterilized filter paper discs (Whatman No.1, 6 mm in diameter) were placed on the surface of the MHA and soaked with 20 µl of a solution of each compound. The inoculated plates were incubated at 37°C for 24 hrs in the inverted position. The diameters (mm) of the inhibition zones were measured. The antibacterial activity results were expressed in term of the diameter of zone of inhibition and <9mm zone was considered as inactive; 9-12mm as partially active; while 13-18mm as active and >18mm as very active [6].

Results and iscussion

Some Physical properties of the ligand and it's metal complexes:

The UV-Vis spectra of Schiff base under study was shown in Table 1: The band at 297 (λ_{max}) due to the (π-π*) transition and band at 328(λ_{max}) due to the (n-π*) transition. Co (II) complex showed band at 329 (λ_{max}) due to the (π-π*) transition and band at 399(λ_{max}) due to the (n-π*) transition. Ni (II) complex show band at 225(λ_{max}) due to (π-π*) transition and band at 321(λ_{max}) due to the (n-π*) transition. Pb (II) complex show band at 236(λ_{max}) duo to the (π-π*) transition and band at 329(λ_{max}) due to the (n-π*) transition.

Table 1: Some properties and UV-Vis spectrum of the ligand and its complexes

Compounds	Ratio	Yield	Color	n-π* (nm)	π-π* (nm)
Ligand	1:1	64.19%	White	328	297
Co(II) complex	1:2	51.43%	Reddish	399	329
Ni(II) complex	1:2	63.88%	Green	321	225
Pb(II) complex	1:2	71.30%	Yellow	329	236

IR Spectra of the ligand and its metal complexes

The IR spectra of the ligand and its metal complexes are shown in table 2: The IR of the ligand and its complexes confirms the formation of Imines bond (-C=N-H) and the absences of carbonyl bond (C=O). The strong bands in the spectra between 3250 and 3286 cm^{-1} may be assigned to NH_2 [7]. The absence of bonds in region 2650-2500 cm^{-1} in The free ligand indicates absence of S-H group in the free ligand [8]. In the spectrum of the ligand strong band intensity at 779 cm^{-1} can be assigned to pure νC=S [8]. in ligand assigned to C=S [9], which appear at lower frequency (428 - 455)cm^{-1} with the metal complex indicating coordination of thiosulfur atom M-S.

Table 2: IR bands (cm^{-1}) of vanillin thiosemcarbazone and its metal complexes

No	Compounds	Wave number (cm^{-1})						
		ν(OH)	ν(NH_2)	ν(Ar-C-H)	ν(C=N)	ν(N-N)	ν(M-N)	ν(M-S)
1	Ligand	3250	3278	2839-3035	1600	1029	-	-
2	Ni(II) complex	3475	3250	2839-3035	1590	1029	563	435
3	Co(II) complex	3450	3280	2839-3200	1590	1029	563	455
4	Pb(II) complex	3406	3286	2619-3152	1585	1029	543	428

Antimicrobial activity of ligand and its metal complexes

The ligand was inactive against one fungi *Candida albicans* and three type of bacteria (*Escherichia coli, Pseudomonas aeruginosa, Bacillus subtilis*) and partially active against one type of bacteria (*Staphylococcus aureus*). The Ni (II) complex was inactive against four type of bacteria (*Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa, Bacillus subtilis*), and partially active against one fungi *Candida albicans*. The Co (II) complex was active against one type of bacteria (*Escherichia coli*) and one fungi *Candida albicans* and partially active against three types of bacteria (*Pseudomonas aeruginosa, Bacillus subtilis, Staphylococcus aureus*). Pb (II) complex was active against one type of bacteria (*Bacillus subtilis*) and partially active against three types of bacteria (*Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus*). As shown in Table 3.

Table 3: Antimicrobial activity of vanillin thiosemicarbazone and it is metal complexes

Compounds	Gram-ve Bacteria		Gram+ve Bacteria		Fungi
	E. coli	***Ps.a***	***S.a***	***B.s***	***Ca***
Ligand	-	8	9	8	-
Ni (II) complex	8	8	7	7	10
Co (II) complex	13	11	11	12	15
Pb (II) complex	10	10	10	13	\10

Key: <9mm zone was considered as inactive; 9-12mm as partially active; while 13-18mm as active and >18mm as very active.

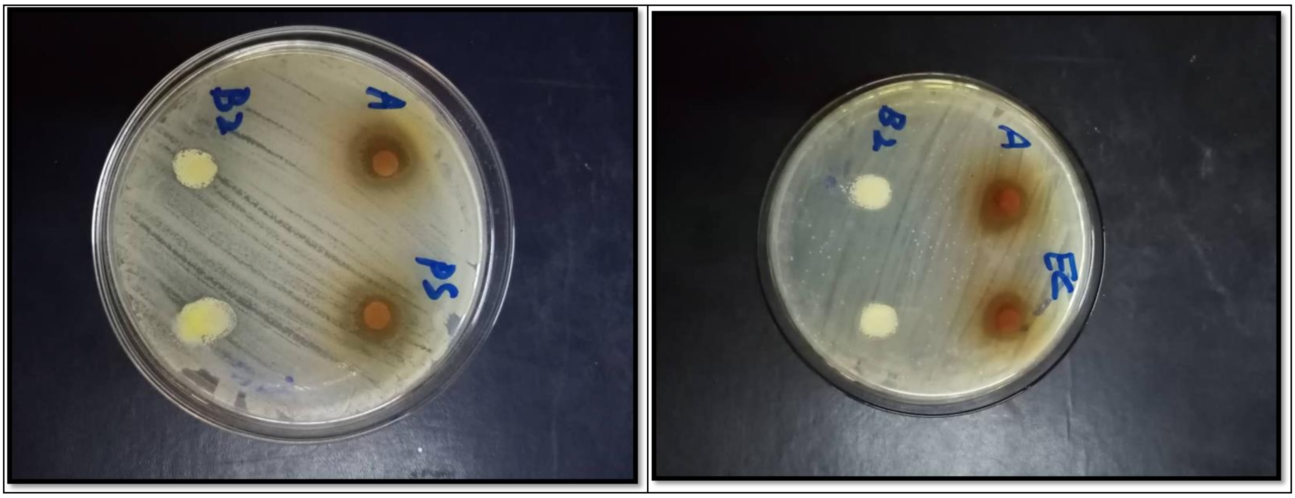


Fig 1: Inhibition zones of Co (II)^{A} and Pb (II)^{B} complexes against *P. aeruginosa and E.coli*

Conclusion

From the IR and UV spectra of the ligand and its metal complexes confirmed that the formation of azomethine group (-C=N-H) and the absences of carbonyl group (C=O), also the formation of (M-N) and (M-S) bonds at all metal complexes, this confirms that the ligand is neutral bidentate ligand coordinated via azomethine N and thione S all metal ions, and all the metal complexes were four coordinated. Also concluded that the free ligand was inactive against (*Candida albicans)* and tree types of bacteria (*E. coli, Pseudomonas. aeruginosa, and Bacillus subtilis*) and partially active against one type of bacteria (*Staphylococcus aureus*), Ni (II) complex was inactive against four type of bacteria (*Bacillus subtilis, Staphylococcus aureus*, and *E. coli* and *Pseudomonas. aeruginosa*). and partially active with fungi (*Candida albicans),* Co (II) complex was active against one type of bacteria (*E. coli*) and fungi (*Candida albicans),* partially active against three type of bacteria (*Bacillus subtilis, Staphylococcus aureus*, and *Pseudomonas aeruginosa*), Pb (II) complex was active against one type of bacteria(*Bacillus subtilis*) and partially active with three type of bacteria(*Staphylococcus aureus, E. coli* and *Pseudomonas. aeruginosa*).

Disclosure statement

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

Author contributions: All authors contributed equally to this work.

Ethical approval: All ethical guidelines have been adhered.

Sample availability: Samples of the compounds are available.

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