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Synthesis, Characterization and Antimicrobial Studies on The Co(II), Ni(II) and Cu(II) Metal Complexes with Schiff Base and Heterocyclic Amines

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Abstract: Some Schiff base complexes of Co(II), Ni(II) and Cu(II) containing heterocyclic amines has been prepared. The complexes were isolated from the reaction in solid forms and characterized by IR, UV- Vis., and some physical measurements. The magnetic susceptibility measurement showed that the complexes of Co(II) and Cu(II) were paramagnetic in nature while the Ni(II) was diamagnetic. The complexes have been found to have moderate to strong antimicrobial, antifungal and cytotoxic activities.

Keywords: *Transition metal complex; Heterocyclic amine; Antimicrobial activity; Schiff base*

Introduction: Many complexes of different Schiff bases have been reported by a number of authors [1-7]. These complexes have attracted special attention due to their wide range of applications in analytical chemistry, [8] biological and industrial fields [9]. Sharma et. al. [10] worked on some Iridium (III) complexes derived from Schiff base and amino carboxylic acids and characterized them by some modern techniques. Ahmed et al. [11] prepared complexes of Ni (II) with Schiff base derived from the condensation of 7-hydroxy-5-methoxy-2-methyl amino acids. Complexes of Zr(IV) and Ti(III) with tridentate Schiff base derived from glycine and salicyldehyde and amine bases were studied by Islam et al. [12], Tarafder et. al. [13] studied the thiocyanato complexes of Ni(II), Co(II) and Zn(II). These kinds of Schiff base ligands provide intriguing chemistry with both the lighter and heavier transition metals. In this work, we report the synthesis, characterization and antimicrobial activity of Ni(II), Co(II) and Cu(II) metal complexes with Schiff base and heterocyclic amines to observe the antimicrobial activity of metal complexes with Schiff base and heterocyclic amines.

Materials & Method:

Reagents and Chemicals: All the reagents used were of analar or chemically pure grade. Solvents were purified and dried according to standard procedures

Physical Measurements: The melting or decomposition temperatures of all the prepared metal complexes were observed in an electro thermal melting point apparatus model No.AZ6512. The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance was used for the present investigation. Infrared disc were recorded in a SIMADZU FTIR-8400 (Japan) infrared spectrophotometer, from 4000-400 cm^{-1} using KBr as binding materials. The absorbance of the complexes were recorded on SHIMADZU UV-2100 spectrophotometer.

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General Synthesis Method for Schiff Bases (SB): The Schiff bases were synthesized by the condensation of salicyldehyde with O-aminophenol. Salicylaldehyde (1.7g, 0.014mol) in absolute ethanol (20 mL) was added to an ethanolic solution of O-aminophenol (0.014 mol). The mixture was heated to reduce the volume to 25 mL, and then it was cooled in an ice bath. The colored product was isolated and washed with hot ethanol and dried in a vacuum desiccator over anhydrous $CaCl_2$.

General method for the preparation of complexes*:* General formula: [M(SB)L]; Where, M=Co(II), Ni (II) and Cu(II). L=Heterocyclic amines/ Quinoline, Iso-quinoline, 2-picoline and 4-picoline. 0.002 mol of metal salt, 0.002 mol of SB and 0.004 mol of KOH were separately dissolved in ethanol and then the solution were mixed and heated on a water bath for half an hour.

Then an ethanolic solution of 0.002 mol of "L" was added to the mixed solution. The resultant mixture solution was heated under reflux on a water bath for 2hours and then cooled. The coloured precipitate so formed was filtered, washed with hot ethanol and dried in a vacuum desiccator over anhydrous $CaCl_2$.

The formation of the complexes can be shown by the following reactions:

$$H_2L' + 2KOH \longrightarrow K_2L' + 2H_2O$$

$$MCl + K_2L' + L \longrightarrow ML'L + 2KCl$$

Where, M= Co(II), Ni(II) and Cu(II).

H_2L' = Schiff bases (SB) L' = Deprotonated Schiff bases

L= Heterocyclic amines e,g, Quinoline, Isoquinoline, 2-Picoline and 4-Picoline.

Results and Discussion:

Physical properties of the complexes: The physical properties of the complexes are given in **Table 1**. The molar conductance in DMSO indicates that the metal complexes are nonelectrolyte in nature. The magnetic susceptibility measurement showed that the complexes of Co(II) and Cu(II) were paramagnetic in nature and the Ni(II) was diamagnetic.

Table 1. Physical properties of the complexes

Complex	Colour	Melting point	Molar Conductance $Ohm^{-1}Cm^2mol^{-1}$	Magnetic moment μ_{eff} (B.M.)
[Co(SB)Q]	Black	210	2.0	1.86
[Co(SB)IQ]	Brown	245	2.1	1.73
[Co(SB) (2-Pic)]	Ash	230	3.0	1.89
[Co(SB)(4-Pic)]	Brown	229	2.4	1.98
[Ni(SB)Q]	Greenish yellow	280	2.2	Dia
[Ni(SB)IQ]	Red	235	2.4	Dia
[Ni(SB) (2-Pic)]	Green	260	2.6	Dia
[Ni(SB)(4-Pic)]	Greenish	240	2.9	Dia
[Cu(SB)Q]	Green	225	2.1	1.87
[Cu(SB)IQ]	Black	210	6.1	1.98
[Cu(SB) (2-Pic)]	Deep green	240	3.9	1.90
[Cu(SB)(4-Pic)]	Blue	220	4.5	2.10

Where, SB: $C_{13}H_9NO_2H_2$, Q : Quinoline, IQ : Iso-quinoline, 2-Pic : 2-Picoline and 4-Pic : 4-Picoline

Electronic spectra of the complexes: The UV-vis spectra of the complexes [Co(SB)L] in Table 2 showed three absorption bands at 480, 540, 580 nm respectively. The compound [Ni(SB))L] showed absorption at 420, 362, and 320 nm which correspond to $^1A_{2g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$ transitions in D_{4h} symmetry, respectively. The UV-vis spectrum of the complexes [Cu(SB)L] showed three absorption bands at 410, 640, nm for $^2B_{1g} \rightarrow {}^2A_{1g}$ and charge transfer transition respectively. The electronic spectral data of the complexes showed bands between 230-360 nm regions due to the charge transfer band only.

Table 2. Electronic spectral data of few complexes

Complexes	Band-I	Band-II	Band-III
[Co(SB)L]	480	540	580
[Ni(SB)L]	320	362	420
[Cu(SB)L]	410	480	640

Where, SB: $C_{13}H_9NO_2H_2$, L : Quinoline,/Iso-quinoline/ 2-Picoline / 4-Picoline

IR Studies of the complexes: The infrared spectral data have been given in Table 3. The Schiff base ($C_{13}H_9NO_2H_2$) behaves as tridentate di-negative ligand coordinating at the imino nitrogen and two oxygen atoms. In the complexes, the shift of ν(C=N) mode to lower frequencies i.e., (1550-1610) cm^{-1} indicates that bond formation takes place through the imino nitrogen atom.

The ν(O-H) band observed in the free Schiff base disappears upon coordination, which indicates deprotonation, and coordination at the oxygen site. Furthermore, the presence of ν(M-O) and ν(M-N) linkages of bands at (535-505) and (415-400) cm^{-1}, respectively were observed for all the complexes.

Table 3. IR spectral data of few metal complexes

Complexes	ν(C=N) cm^{-1}	ν_{asym} (C-H) of aromatic cm^{-1}	ν(M-O) cm^{-1}	ν(M-N) cm^{-1}	ν(O-H) cm^{-1}
Ligand/(SB)	1632	-	-	-	3415
[Co(SB)L]	1610	3040	535	415	-
[Ni(SB)L]	1580	3000	520	410	-
[Cu(SB)L]	1550	3100	505	400	-

Where, SB: $C_{13}H_9NO_2H_2$, L : Quinoline,/Iso-quinoline/ 2-Picoline / 4-Picoline

Antibacterial, antifungal and cytotoxic activity of the metal complexes: The disc diffusion technique is widely acceptable for preliminary investigations of compounds, which are suspected to possess antimicrobial properties. Antimicrobial activities of the test samples are expressed by measuring the zone of inhibition observed around the area. The present results revealed that the complexes are more microbial toxic than the free metal ions or ligands. The metal Schiff bases complexes (Table 4) showed moderate to strong activity against both Gram positive and Gram negative bacteria compared to standard Kanamycin. The results of the antifungal activity of the complexes are recorded in Table-5. The highest antifungal activity was shown in the complex [Ni(SB)(4-Pic)] against Candida albicaus (8mm). Brine Shrimp lethality bioassay is a development in the bioassay for the bioactive compounds. Here, *in vivo* lethality in a simple zoological organism (brine shrimp nauplii) is used as a convenient monitor for screening and fractionation in the discovery of new bioactive products. In this bioassay, the mortality rate of brine shrimp was found to increase with the increase of concentration of the samples. The test complexes showed positive results in brine shrimp lethality bioassay. So these complexes are bioactive (Table 6).

Table 4. Antibacterial activity of the complexes and Kanamycin

Complexes	Zone of inhibition, diameter in nm			
	Gram Negative		Gram Positive	
	E. coli	Shigella dysenteriae	Agro bacterium	Bacillus subtilis
[Ni(SB)2-Pic]	10	06	06	07
[Co(SB)(4-Pic)]	07	08	05	08
[Cu(SB)4-pic]	07	07	07	06
Kanamycin -30	28	20	21	25

Table 5. Antifungal activity of the complexes against Saccharromycess(SC), Aspergillus niger (AN), Candida albicaus(CA)

Complexes	Diameter of zone inhibition (mm) 200µg/disc		
	SC	AN	CA
[Co(SB)(4-Pic)]	0	0	0
[Ni(SB)IQ]	vp	vp	vp
[Ni(SB) (2-Pic)]	vp	vp	vp
[Ni(SB)(4-Pic)]	0	6	8
[Cu(SB)(4-Pic)]	8	vp	vp

Where vp = very poor

Table 6. Brine shrimp lethality bioassay for test complexes

Complexes	24h Exposure
	LC_{50} (µg/mL)
[Ni(SB)(2-pic)]	12.58
[Cu(SB)(4-Pic)]	15.13
[Co(SB-)(4-Pic)]	12.12

Conclusions: Synthesis and characterization of Some Schiff base complexes of Co (II), Ni(II) and Cu(II) containing heterocyclic amines have been presented in this paper. The present results revealed that the complexes are more microbial toxic than the free metal ions or ligands. The results of the antibacterial screening of the test compounds indicate mild to moderate bactericidal activities against both Gram positive and Gram negative bacteria compared to standard Kanamycin. Among all prepared complexes, The highest antifungal activity against Candida albicaus (8 mm) was shown by the complex [Ni(SB)(4-Pic)]. All obtained complexes are bioactive as they showed positive results in brine shrimp lethality bioassay.

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