

Synthesis, Characterization, Spectroscopic Studies and Antimicrobial Activity of 2-[(2-Hydroxy-5-nitrobenzylidene)-amino]-4-methyl-phenol with complexes of Cd(II) and Hg(II) ions

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Abstract: A new Schiff base complexes derived from 2-amino, 4-methyl phenol with 5-nitro salicylaldehyde (AMPNSA). The metal chelates were prepared and characterized by IR, UV-Vis and NMR spectroscopy, Elemental analysis and Molar conductance measurements. The Schiff base and its metal chelates have been tested for their antimicrobial activity using disc diffusion methods and the results discussed.

Keywords: Schiff base, Metal chelates, Spectral studies and Anti-microbial activity.

INTRODUCTION

Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions^{1,2}. Many biologically important Schiff bases have been reported in the literature possessing antibacterial³, antifungal and anti-HIV^{4,5}, herbicidal⁶, antitubercular⁷ and anticancer activities⁸. Receiving impetus from above observation, it was thought worthwhile to synthesize transition metal chelates of 2-[(2-Hydroxy-5-nitrobenzylidene)-amino]-4-methyl-phenol with Cd(II) and Hg(II) metal ions.

EXPERIMENTAL

Materials and Methods

All the chemicals and solvents used in the present work were of analytical grade. The metals were used as their chloride salts. Elemental analysis was done on instrument Eager-300 analyzer. Infrared

and UV spectra were recorded on Perkin Elmer spectrum 100 and UV-Vis spectrophotometer 119 in the 200-1000 nm ranges in DMF solution (10^{-3}). Conductance of the metal complexes was determined in DMF on conductivity meter Equip-tronics model No-EQ665. Melting points were recorded by open capillary method and are uncorrected. ¹H-NMR spectra of Schiff base and its metal complexes recorded on Bruker 300 MHz spectro meter in DMSO-d₆.

The antimicrobial activities of Schiff base and their metal chelates were screened by Disc Diffusion method.

Synthesis of Schiff base (AMPNSA)

Schiff base was prepared by condensing of 2-amino, 4-methyl phenol and 5-nitro salicylaldehyde with 0.01M were mixed in 1:1 ratio and refluxed on water bath for 2-3 hours in presence of glacial acetic acid. The reaction mixture was poured in ice. Brown orange precipitate appears. Resultant

precipitate was filtered by suction, and washing with distilled water and ethyl alcohol.

Then dried in vacuum dessicator, purity of ligand was checked by TLC. The structure of Schiff base was interpreted by Infrared spectra, Elemental analysis and NMRspectral analysis.

Synthesis of Metal Chelates

The cadmium chloride 0.01M solution was prepared in ethyl alcohol. Also, 2-[(2-Hydroxy-5-nitrobenzylidene)-amino]-4-methyl-phenol 0.01M solution was prepared in warm ethanol. The metal ion solution added to the ligand solution with constant stirring.

The P^H of the reaction mixture was adjusted 6.9 to 7.1 by adding alcoholic ammonia drop by drop. Then the reaction mixture was refluxed for four hours on water bath. Orange red precipitate was allowed to settle down. The precipitate is filtered through whatmann paper. The complex was purified by distilled water and ethyl alcohol. The complex is dried in dessicator and yield was recorded.

RESULTS AND DISCUSSION

Analytical data and physical properties of ligand and metal complexes are given in Table No.1. The metal complexes were intense coloured, insoluble

in common organic solvents but soluble in DMF, DMSO. For the estimation of chloride by Volhard's method is used⁹, metal ion percentage is determined by standard method¹⁰.

Presence of lattice water molecule present in the complex was recorded by keeping the known weight of the complex in previously weighed crucible in oven at 110°C for one hour. The difference in weight gives the amount of lattice water in the complex.

The compounds give satisfactory elemental analysis. Values are in close agreement with the values calculated for expected molecular formulae assigned to these complexes, suggesting 1:1 for Cd(II) and Hg(II) complexes. The molar conductance of Cd(II) complex in DMF reveal its electrolytic nature¹¹, and Hg(II) complex indicates non electrolyte nature¹².

Electronic Spectra

The UV electronic spectra of Cd(II) and Hg(II) complexes indicates, the transition is shifted towards higher or lower frequencies which confirm the coordination of the ligand to the metal ions. Also, electronic spectra of Cd(II) and Hg(II) complexes display absorption band at 28129cm⁻¹ and 27777cm⁻¹ assigned as charge transfer band^{13,14}.

Table No.1: Analytical data and physical properties of Schiff base (AMPNSA) and their metal chelates.

Ligand / Metal Chelates Empirical Formula	Mol. Wt.Colour / D.P ^o C	M:L Ratio/ Yield (%)	Molar Cond. (Ω ⁻¹ cm ² mol ⁻¹)	Elemental analysis % Cal (Obs)				
				C	H	N	M	Cl
AMPNSA C ₁₄ H ₁₂ N ₂ O ₄	272.72 Brown Orange (166)	- 88	-	61.60 (60.05)	4.40 (4.32)	10.26 (10.31)	-	-
[Cd(AMPNSA) H ₂ O]Cl C ₁₄ H ₁₃ N ₂ O ₅ ClCd	436.90 Orange Red (292)	1:1 63	48	38.45 (38.01)	2.97 (2.35)	6.40 (6.89)	25.72 (25.21)	8.12 (8.00)
[Hg(AMPNSA)Cl] H ₂ O C ₁₄ H ₁₃ N ₂ O ₅ ClHg	525.09 Brown grey (299)	1:1 56	13	31.99 (31.45)	2.47 (2.19)	5.33 (5.24)	38.20 (38.00)	6.76 (6.21)

Infrared Spectra

The IR spectra of Schiff base ligand AMPNSA exhibit a band in the region at 3090cm^{-1} due to $\nu(\text{OH})$. This band is disappeared in the complexes, indicating deprotonation of this group¹⁵. Similarly a band observed around 1389cm^{-1} is due to the bond bending vibration of $-\text{OH}$ group shifted at 1370cm^{-1} to 1374cm^{-1} in metal complexes, suggesting the involvement in metal coordination. This is further reflected by the appearance of phenolic $\nu(\text{C}-\text{O})$ at 1269cm^{-1} in ligand. This band in the complexes was shifted to higher stretching frequency¹⁶.

Further, the band observed at 1625cm^{-1} due to $\nu(\text{C}=\text{N})$ azomethine group in ligand is shifted towards lower frequency by $15\text{-}20\text{cm}^{-1}$ in the spectra of complexes indicate, that azomethine group involved in coordination with metal ion¹⁷.

New band at 3424cm^{-1} Cd(II) complex suggesting the presence of coordinated water molecule¹⁸. The appearance of new bands in the

spectra of Cd(II) and Hg(II) metal ion complexes at $474\text{-}476\text{cm}^{-1}$ and $548\text{-}560\text{cm}^{-1}$ due to new bonding i.e, $\nu(\text{M}-\text{N})$ ⁴² and $\nu(\text{M}-\text{O})$ ⁴³.

¹H NMR Spectra

The ¹H-NMR spectrum of the ligand AMPNSA indicated signals at δ 2.23 ppm (s) for methyl protons, δ 6.8-7.59 (m, 7H) due to aromatic protons, δ 8.10 ppm (s, 1H) for azomethine proton, δ 9.41 (s, 1H) Ar-OH²¹ and δ 13.30 (s, 1H) for Ar-OH.

In Cd(II) and Hg(II) complexes phenolic $-\text{OH}$ peak have been shifted to down field at δ 10.21 ppm and δ 10.35 ppm respectively. A signal corresponding to azomethine in free ligand at δ 8.10 ppm is shifted to down field region in metal complexes²². The disappearance of peak at δ 13.30 ppm due to phenolic OH may be attributed to deprotonation of this group on involvement in bonding²³.

A new peak observed at δ 2.0 ppm in Cd(II) complex due to corresponding water molecule²⁴.

Table No.2: Infrared spectral data of ligand (AMPNSA) and their metal chelates.

Compounds	$\nu(\text{H}_2\text{O})$	$\nu(\text{OH})$	$\nu(\text{OH})$	$\nu(\text{C}-\text{O})$	$\nu(\text{CH}=\text{N})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
AMPNSA	-	3090	1389	1269	1625	-	-
[Cd(AMPNSA)H ₂ O]Cl	3424	-	1374	1281	1607	476	548
[Hg(AMPNSA)Cl]H ₂ O	-	-	1370	1280	1615	474	560

Proposed structures for the metal complexes:

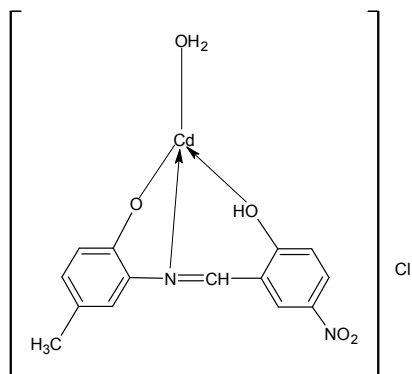


Figure 1

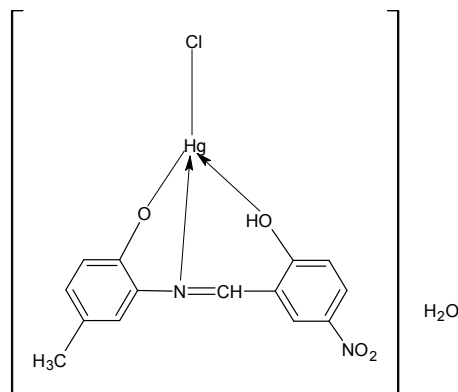


Figure 2

On the basis of the above observation it is therefore, proposed that [Cd(II) AMPNSA] and [Hg(II) AMPNSA] complexes shows tetrahedral geometry in which ligand (AMPNSA) behave as uninegative tridentate in nature.

ANTIMICROBIAL ACTIVITY

Synthesized Schiff base (AMPNSA) and their metal complexes were screened against *Escherichia coli*, *Bacillus subtilis*, *Aspergillusflavus* and *Aspergillusniger* to assess their potential as antimicrobial agent by Disc Diffusion method²⁵. The zones of inhibition based upon zone size around discs

were measured. The measured zone of inhibition against the growth of various microorganisms is listed in Table No.3 and 4.

The [Cd(II) AMPNSA] and [Hg(II) AMPNSA] complexes have more zone of inhibition towards *Escherichia coli* and *Bacillus subtilis*. 2-[(2-Hydroxy-5-nitrobenzylidene)-amino]-4-methyl-phenol (AMPNSA) produces zone of inhibition 6 mm for *Aspergillusflavus* and negative zone for *Aspergillusniger*. The result indicates that Cd(II) and Hg(II) metal complexes form zone of inhibition towards *Aspergillusflavus* and *Aspergillusniger*.

Table No.3: Result of antibacterial study of Cd(II) and Hg(II) complexes

Sr. No.	Compounds	<i>Escherichia coli</i>	<i>Bacillus subtilis</i>
1	AMPNSA	8 mm	6 mm
2	[Cd(II) AMPNSA]	15 mm	6 mm
3	[Hg(II) AMPNSA]	12 mm	31 mm
4	Streptomycin	24 mm	30 mm
5	Control (DMSO)	10 mm	14 mm

-ve –No antibacterial activity, zone of inhibition -----mm.

Table No.4: Result of antifungal study of Cd(II) and Hg(II) complexes

Sr. No.	Compounds	<i>Aspergillusflavus</i>	<i>Aspergillusniger</i>
1	AMPNSA	6 mm	-ve
2	[Cd(II) AMPNSA]	7 mm	7 mm
3	[Hg(II) AMPNSA]	36 mm	25 mm
4	Fluconazole	15 mm	10 mm
5	Control (DMSO)	-ve	-ve

-ve –No antifungal activity, zone of inhibition -----mm.

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