

RESEARCH ARTICLE

ANALYTICAL CHEMISTRY

SYNTHESIS, CHARACTERIZATION, SPECTRAL STUDIES AND ANTIMICROBIAL ACTIVITY OF 2-[1-(2-HYDROXY-PHENYL)-ETHYLIDENE AMINO]-4-METHYL-PHENOL WITH COMPLEXES OF CD(II) AND HG(II) IONS

SURAJ B. ADE^{1*}, M.N. DESHPANDE² AND D.G. KOLHATKAR²

^{1*}Department of Chemistry, Shri Shivaji College, Parbhani-431401, India

²P.G. Department of Chemistry, NES, Science College, Nanded-431605, India



SURAJ B. ADE

Department of Chemistry, Shri Shivaji College, Parbhani-431401, India

ABSTRACT

Transition metal (II) complexes of the type ML_1 [where $M=Cd(II)$ and $Hg(II)$, L_1 =Schiff base derived from 2-amino, 4-methyl phenol and O-hydroxy acetophenone] have been prepared, characterized by elemental analysis, molar conductivity, IR, electronic spectra, NMR spectral and X-ray diffraction studies. Molar conductivity measurements indicate that the complexes are non-electrolyte in nature. The analytical data confirm metal to ligand ratio in the complexes were 1:1. IR spectral data suggests that the ligand (AMPOHA) behaves as tridentate ONO donor system. X-ray diffraction studies determine monoclinic crystal system for these complexes. The Schiff base and their metal complexes have been tested for their antibacterial and antifungal activity using disc diffusion methods.

KEYWORDS

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

INTRODUCTION

Schiff bases metal complexes play important roles in coordination chemistry. Schiff base and the relevant transition metal complexes are still found to be of great in inorganic chemistry although this subject has been studied extensively¹⁻². Schiff bases are most widely used as chelating ligands in coordination chemistry and investigated extensively for the last several decades leading to new synthetic routes of structural³, biological⁴ and industrial applications⁵. They are also useful in catalysis and in medicine as antibiotics, antiallergic and antitumor agents⁶⁻⁸. Tridentate ligands extensively studied contain the ONO donor atoms that form strong covalent bonds with nitrogen⁹. The metal chelates containing O, N donor atoms are very important owing to their significant antibacterial and anticancer activity^{10, 11}. Receiving impetus from above observation, it was thought worthwhile to synthesize transition metal chelates of 2-[1-(2-Hydroxy-phenyl)-ethylidene amino]-4-methyl-phenol with Cd(II) and Hg(II) metal ions.

MATERIALS AND METHODS

All the chemicals and solvents used were A.R. grade. The metals were used as Cd(II)Cl₂ and Hg(II)Cl₂. CHN analysis was done on instrument Egar-300 analyzer. IR and UV-Vis spectra were recorded on Perkin Elmer Spectrum 100 and UV-Vis spectrophotometer 119 in the 200-1000 nm range in DMF solution (10⁻³).

Conductance of the metal chelates 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 spectral analysis on Bruker 300 MHz spectrometer in DMSO-d₆.

Powder XRD diffractograms of the complexes were obtained from CFC Shivaji University, Kolhapur on Philips Analytical XRD B.V. Spectrophotometer in the 2θ range from 10 to 90° and results are then indexed to assign the crystal system. The antimicrobial activities of Schiff base and their metal chelates were screened by Disc Diffusion method.

Synthesis of Schiff base (AMPOHA)

Schiff base (AMPOHA) was prepared by condensing 2-amino, 4-methyl phenol and O-hydroxy acetophenone with 0.01M mixed in 1:1 ratio. The reaction solution was refluxed on water bath for 2-3 hours in presence of glacial acetic acid. The resulting reaction mixture was poured in crushed ice, and a dark green precipitate formed. Then it is filtered by suction and purified with distilled water and ethanol. Further it is dried in vacuum desiccator and recrystallized from ethanol, and the purity of the Schiff base was checked by TLC. The structure of Schiff base was interpreted by Infrared spectra, Elemental and NMR spectral analysis.

Synthesis of Metal Chelates

To a 50ml solution of metal chloride (0.01M) in ethanol, 50ml warm ethanolic solution (0.01M) of AMPOHA was added drop wise with constant stirring. P^H of the reaction mixture was maintained about 6.5 to 6.9 by adding alcoholic ammonia drop by drop. The resultant reaction mixture refluxed for about 5 to 6 hours on water bath.

Grey black precipitate appears, and was allowed to digest and filtered off. Resultant solid complex was washed with distilled water and

warm ethanol, dried in dessicators and stored in bottles.

RESULTS AND DISCUSSION

All the metal chelates were coloured, they were soluble in DMF, DMSO. All the results of elemental analysis are given in Table No.1. For the estimation of chloride Volhard's method is used¹². Metal ion percentage is determined by standard method¹³.

Presence of lattice water molecules present in the metal complexes 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 molecule in the complex.

All 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) and Hg(II) complexes in DMF reveals their non-electrolyte nature¹⁴.

Table No.1

Analytical data and physical properties of (AMPOHA) ligand and its metal complexes.

Ligand / Metal Complexes Empirical Formula	Mol. Wt. Colour/ (D.P ^o C)	M:L Rati o/Yi eld (%)	Molar Cond. (Ohm ⁻¹ cm ² mol ⁻¹)	Elemental analysis % Cal (Obs)				
				C	H	N	M	Cl
AMPOHA C ₁₅ H ₁₅ NO ₂	241.30 Dark green (161)	- 60	-	74.59 (74.65)	6.21 (6.35)	5.80 (5.89)	-	-
[Cd(AMPOHA) Cl] H ₂ O C ₁₅ H ₁₆ NO ₃ ClCd	405.90 Grey black (>300)	1:1 54	9.1	44.34 (44.21)	3.94 (3.71)	3.44 (3.22)	27.69 (27.79)	8.74 (8.71)
[Hg(AMPOHA) Cl] H ₂ O C ₁₅ H ₁₆ NO ₃ ClHg	494.09 Grey black (>300)	1:1 56	9.7	36.43 (36.35)	3.23 (3.14)	2.83 (2.94)	40.59 (40.19)	7.18 (7.11)

Ligand AMPOHA exhibits strong absorption band at 30303cm⁻¹ due to n→π* transition. Electronic spectra of Cd(II) and Hg(II) complexes display absorption bands at 30030cm⁻¹ and 30864cm⁻¹ assigned to charge transfer band¹⁵.

The IR spectra of chelating agent 2-[1-(2-Hydroxy-phenyl)-ethylidene amino]-4-methylphenol (AMPOHA) exhibits a medium strong intensity band at 3375cm⁻¹ due to phenolic -OH and this band shifted to lower side at 3371cm⁻¹ in Cd(II) complex and 3369cm⁻¹ in Hg(II) complex, suggesting that the chelation through

phenolic –OH without deprotonation. Another important ligand band, occurring at about 1373cm^{-1} due to phenolic –OH group of acetophenone moiety. Absence of this group in the complexes indicates the deprotonation of phenolic –OH on coordination with metal¹⁶. A band at 1229cm^{-1} due to phenolic C-O shifts to higher frequency in both the complexes¹⁷. A

medium intensity band in ligand spectra at 1605cm^{-1} is attributed to ν (C=N) azomethine mode, this band has shifted to higher frequency at 1617cm^{-1} and 1620cm^{-1} in both the complexes¹⁸.

The new weak bands $521\text{-}543\text{cm}^{-1}$ and $570\text{-}615\text{cm}^{-1}$ due to new bonding i.e, $\nu(\text{M-N})$ ¹⁹,
²⁰ and $\nu(\text{M-O})$ ²¹⁻²²

Table No.2
Infrared spectral data of ligand (AMPOHA) and their metal complexes

Compounds	$\nu(\text{OH})$ Phenolic	$\nu(\text{OH})$ Aceto- phenone moiety	$\nu(\text{C-O})$	$\nu(\text{C=N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
AMPOHA	3375	1373	1229	1605	-	-
[Cd(AMPOHA)Cl]H ₂ O	3371	-	1243	1617	521	570
[Hg(AMPOHA)Cl]H ₂ O	3369	-	1241	1620	543	615

The ¹H-NMR spectrum of the Schiff base (AMPOHA) shows peaks at δ 2.25ppm corresponding to methyl protons of O-Hydroxy acetophenone and at δ 2.35ppm for methyl protons of (s, 3H) for Ar-CH₃. At δ 5.00ppm (s, 1H) due to Ar-OH of O-Hydroxy acetophenone group, δ 6.16-6.85ppm (m, 7H, Ar-H) and δ 13.30ppm (s, 1H, Ar-OH).

On complexation signals at δ 5.00ppm due to Ar-OH group of O-Hydroxy acetophenone have disappeared²³. In Cd(II) and Hg(II) complexes, the peak at δ 13.30ppm (s, 1H, Ar-OH) in free ligand get shifted to deshielded region and also the methyl protons attached to tertiary nitrogen has been shifted to down field region which shows a peak at δ 2.57ppm.

[Cd(AMPOHA)Cl]H₂O

Crystal system: Monoclinic Lattice Type: P

Radiation: Cu Wavelength: 1.540598 \AA

Lattice Parameter: a = 4.9168 b = 4.9168 c = 5.4089 \AA

Thus AMPOHA molecule seems to be coordinated to the metal ion through phenolic OH, azomethine nitrogen and phenoxide oxygen.

X-ray diffraction study of Cd(II) and Hg(II) metal complexes were scanned in the range $2\theta = 10$ to 90° . With the help of X-ray diffraction technique it is possible, as, certain spatial arrangement of the structural unit substance in investigating the interior of crystal.

The major reflexes were measured and corresponding 'd' values were obtained. Independent indexing, calculation of miller indices and evaluation of lattice parameters a, b, c and angle α , β , γ were done by powder X programme. Data has been summarized in the following tables.

Lattice Parameter: Alpha= 90 Beta= 90 Gama=120⁰
 2Theta Start= 10 2Theta End= 89.98

Table No. 3
Powder XRD data of [Cd(AMPOHA)Cl]H₂O Complex

h	k	l	2θ	2θ	d	d	Intensity
			(Exp.)	(Calc.)	(Exp.)	(Calc.)	(Exp.)
-1	1	1	26.632	26.622	3.34449	3.34573	41.58
-1	1	2	39.444	39.440	2.28266	2.28291	35.82
-1	2	1	40.336	40.263	2.23423	2.23807	36.70
0	2	0	42.454	42.422	2.12752	2.12904	36.48
-2	0	1	45.756	45.763	1.98137	1.98109	32.59
1	1	2	50.187	50.104	1.81633	1.81913	31.01
0	0	3	50.530	50.585	1.80479	1.80297	32.44
0	2	2	54.803	54.835	1.67376	1.67286	26.32
0	1	3	55.306	55.286	1.65970	1.66027	29.50
-2	3	0	57.204	57.191	1.60906	1.60940	27.26

From the X-ray diffraction spectrum of Cd(II) complex cell data and crystal lattice parameters of calculated and tabulated in Table No. 3 indicates that complex has monoclinic crystal system²⁴.

[Hg(AMPOHA)Cl] H₂O

Crystal system: Monoclinic Lattice Type: P
 Radiation: Cu Wavelength: 1.540598 Å⁰
 Lattice Parameter: a= 4.9168 b= 4.9168 c= 5.4089 Å⁰
 Lattice Parameter: Alpha= 90 Beta= 90 Gama=120⁰
 2Theta Start= 10 2Theta End= 89.98

Table No. 4
Powder XRD data of [Hg(AMPOHA)Cl] H₂O Complex

h	k	l	2θ	2θ	d	d	Intensity
			(Exp.)	(Calc.)	(Exp.)	(Calc.)	(Exp.)
-1	1	0	20.870	20.845	4.25288	4.25807	47.88
-1	1	1	26.646	26.622	3.34268	3.34573	47.55
0	0	2	33.194	33.097	2.69674	2.70445	43.99
-1	2	1	40.256	40.263	2.23850	2.23807	40.12
0	2	0	42.335	42.422	2.13320	2.12904	56.31
0	0	3	50.600	50.585	1.80248	1.80297	37.60
-2	1	3	64.013	63.987	1.45336	1.45388	37.79
-3	0	0	65.813	65.737	1.41790	1.41936	35.90
-2	0	3	68.082	68.092	1.37607	1.37589	37.34
-1	0	4	73.380	73.409	1.28924	1.28880	36.44

Cell data and crystal lattice parameters of Hg(II) complex indicates that complex have monoclinic crystal system²⁵ with lattice type-P.

Proposed structures for the metal complexes:

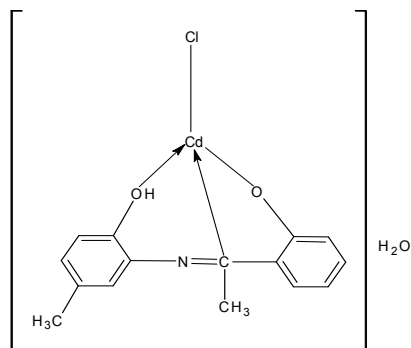


Figure 1

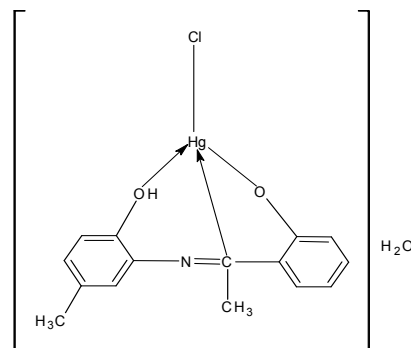


Figure 2

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

ANTIMICROBIAL ACTIVITY

Synthesized Schiff base (AMPOHA) and their metal complexes were screened against Escherichia coli, Bacillus subtilis, Aspergillus flavus and Aspergillus niger to assess their potential as antimicrobial agent by Disc Diffusion method²⁶. 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.5 and 6.

Table No.5
Result of antibacterial study of Cd(II) and Hg(II) complexes

Sr. No.	Compounds	Escherichia coli	Bacillus subtilis
1	AMPOHA	15 mm	11 mm
2	[Cd(II)AMPOHA]	7 mm	6 mm
3	[Hg(II)AMPOHA]	18 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.6
Result of antifungal study of Cd(II) and Hg(II) complexes

Sr. No.	Compounds	Aspergillus flavus	Aspergillus niger
1	AMPOHA	-ve	-ve
2	[Cd(II) AMPOHA]	15 mm	23 mm
3	[Hg(II) AMPOHA]	34 mm	30 mm
4	Fluconazole	15 mm	10 mm
5	Control (DMSO)	-ve	-ve

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

The [Cd(II) AMPOHA] complex produces zone of inhibition 7mm and 6mm towards Escherichia coli and Bacillus subtilis. But [Hg(II) AMPOHA] complex produces more zone of inhibition

towards *Escherichia coli* and *Bacillus subtilis*. The [Hg(II) AMPOHA] complex indicates that it shows more zone of inhibition than the chelating ligand.

The antifungal result indicates that Cd(II) and Hg(II) metal complexes form more zone of inhibition towards *Aspergillus flavus* and *Aspergillus niger*.

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