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Preparation, Chemical Characterization and Electronic Spectra of 6-(2-Pyridylazo)-3-Acetamidophenol and Its Metal Complexes

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**PREPARATION, CHEMICAL CHARACTERIZATION AND
ELECTRONIC SPECTRA OF 6-(2-PYRIDYLAZO)-3-
ACETAMIDOPHENOL AND ITS METAL COMPLEXES**

Key Words : 6-(2-pyridylazo)-3-acetamidophenol complexes, Stability constant determination, IR and magnetic susceptibility, Electronic Spectra

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ABSTRACT

The stereochemistry of new iron (III), cobalt (II), nickel (II), copper (II), zinc (II) and cadmium (II) complexes of 6-(2-pyridylazo)-3-acetamidophenol (H_2L) was studied on the basis of their analytical, spectroscopic, magnetic and conductance data. The dissociation constant of the ligand, as well as the stability constants of its metal complexes had been determined by spectrophotometric method. On the basis of infrared spectra, the coordination behaviour of the ligand to the metal ions was investigated. Magnetic susceptibility and solid reflectance spectra measurements were used to infer the structure. The isolated complexes were found to have the general formulae $[M(HL).xH_2O](A).yH_2O$, $M = Cu(II), Zn(II), Cd(II)$ and $Fe(III)$; $HL = 6-(2-pyridylazo)-3-acetamido-phenol$; $A = acetate$ in the case of $Cu(II)$ and $Zn(II)$ or $chloride$ in the case of $Cd(II)$ and Fe

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(III), $x = 1-3$ and $y=0-5$. For $[M (H_2L).xH_2O]Cl_2.yH_2O$, $M = Ni (II)$ and $Co (II)$; $HL = 6-(2-pyridyl-azo)-3-acetamidophenol$, $x=3$ and $y=5-6$).

INTRODUCTION

A series of α -arylhydrazoneacetylaminopyridine ligand and their copper chelates were prepared and characterized by different tools of analyses¹. New simple and mixed complexes of 1-(2-pyridylazo)-2-naphthol (PAN) or 4-(2-pyridylazo)resorcinol (PAR) were synthesized and characterized²⁻⁴. It was concluded that both PAN and PAR ligands coordinated to the metal ions through the pyridine nitrogen and the o-hydroxyl oxygen⁵⁻⁷. On screening the literature, there is no survey concerning the metal complexes of 6-(2-pyridylazo)-3-acetamidophenol.

The main thrust of this study is to determine the dissociation constant of the 6-(2-pyridylazo)-3-acetamidophenol ligand and the stability constants of its metal complexes. The coordination behaviour of 6-(2-pyridylazo)-3-acetamido-phenol (PAAP) towards transition metal ions is investigated and the data are correlated with their magnetic and conductance properties.

EXPERIMENTAL

Synthesis of the 6-(2-pyridylazo)-3-acetamidophenol (PAAP)

2-Aminopyridine (0.1 mole) was mixed with HCl (0.1 mole) and diazotized below 5 °C with $NaNO_2$ (0.1 mole). The resulting diazonium chloride was coupled with an alkaline solution of 3-acetamidophenol (0.1 mole) below 5 °C. The product was separated by filtration, purified by crystallization from Et_2O and dried over vacuo over anhydrous calcium chloride. The melting point of the solid product was 82 ± 2 °C. The microanalyses for C, H and N was: Calc. (C) 60.9, (H) 4.6, (N) 21.87, M.W. 256; found (C) 60.07, (H) 4.3, (N) 21.7, M.W 256. The IR spectrum revealed the presence of ν (OH), ν (NH) and ν (C=O), ν (C-N) and ν

(N=N) bands of the phenolic OH, acetamide NH, pyridine ring and azo groups at 3566, 3398, 1321, 1522 and 1699 cm^{-1} , respectively. Also, the structure of the ligand was confirmed by $^1\text{H-NMR}$ spectra which give signals at $\delta = 2.526$ ppm (s, 3H, NHCOCH_3), $\delta = 6.19\text{--}8.08$ ppm (m, 6H, ArH's and pyridine H's), $\delta = 10.45$ ppm (s, 1H, OH) and 14.0 ppm (s, 1H, NH). The signals due to the phenolic OH and acetamide NH protons were lost after D_2O exchange.

Synthesis of the complexes

Ammoniacal solution of the appropriate metal chloride or acetate (0.01 mole) in ethanol-water mixture (1:1) (25 ml) was added to the solution of the azo compound (0.01 mole) in the same solvent (50 ml). The resulting mixture was stirred under reflux for one half-hour where upon the complexes were precipitated. They were removed by filtration, washed with 1:1 ethanol:water mixture, and with Et_2O .

The analytical data were collected in Table (1). IR spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer. The solid reflectance spectra were measured on a Shimadzu 3101 PC spectrophotometer. The molar magnetic susceptibilities were measured on powdered samples using the Faraday method. The diamagnetic corrections were made by Pascal's constant. $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as calibrant. Spectrophotometric measurements were carried out using Milton Roy spectrophotometer Model 601. pH measurements were carried out using Schott-Gerate pH meter Model 820. The conductance measurements were carried out using Sybron-Barnstead conductometer.

Metal contents were determined by titration against standard EDTA after complete decomposition of the complexes with aqua regia several times in a Kjeldahl flask.

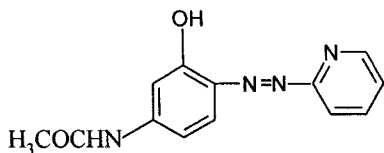
RESULTS AND DISCUSSION

Ligand dissociation constant and metal complexes stability constants

The structure formula of the ligand (PAAP) is given by

TABLE I
Analytical and physical data of 6-(2-pyridylazo)-3-acetamidophenol and its complexes.

Compound	Colour (% yield)	M. P °C	Found (calcd.) %			Molecular wt.		μ_{eff} (B.M.)	Conductance $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
			C	H	N	M	found (Calcd.)		
Ligand $[\text{H}_2\text{L}]$	Red (70)	80 (60.9)	60.07 (60.9)	4.3 (4.6)	21.7 (21.87)		256 (256)	---	---
$[\text{Fe}(\text{C}_{13}\text{H}_{11}\text{N}_4\text{O}_2)(\text{H}_2\text{O})_2]\text{Cl}_2$	Black (70)	>300 (35.8)	37.05 (35.8)	5.1 (3.9)	13.2 (12.84)	13.3 (12.84)	440 (436)	4.29	455
$[\text{Co}(\text{C}_{13}\text{H}_{13}\text{N}_4\text{O}_2)(\text{H}_2\text{O})_3]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	Dark red (63)	>300 (30.4)	29.2 (30.4)	4.9 (5.8)	10.78 (10.9)	11.34 (11.53)	511 (512)	5.0	238
$[\text{Ni}(\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_2)(\text{H}_2\text{O})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$	Rose (60)	>300 (28.5)	27.9 (28.5)	5.9 (6.0)	10.13 (10.23)	10.3 (10.8)	551 (548)	3.82	161
$[\text{Cu}(\text{C}_{13}\text{H}_{11}\text{N}_4\text{O}_2)(\text{H}_2\text{O})_3](\text{OAc}) \cdot 5\text{H}_2\text{O}$	Dark Red (73)	>300 (32.13)	34.6 (32.13)	5.2 (4.73)	11.15 (11.53)	12.7 (13.08)	495 (485.5)	1.89	117
$[\text{Zn}(\text{C}_{13}\text{H}_{11}\text{N}_4\text{O}_2)(\text{H}_2\text{O})_3](\text{OAc}) \cdot 2\text{H}_2\text{O}$	Dark red (73)	>300 (41.4)	40.4 (41.4)	5.0 (4.8)	12.89 (12.93)	14.95 (15.01)	437 (433)	Diam.	125
$[\text{Cd}(\text{C}_{13}\text{H}_{11}\text{N}_4\text{O}_2)(\text{H}_2\text{O})_3]\text{Cl} \cdot 5\text{H}_2\text{O}$	Brown (73)	>300 (30.5)	29.5 (30.5)	3.8 (4.6)	10.9 (10.96)	21.76 (21.93)	511 (510.5)	Diam.	67

6-(2-pyridylazo)-3-acetamidophenol (H_2L)

The structure of this new azo ligand was established by using different tools of analyses, for example, elemental analyses (C, H, N), IR, 1H -NMR and mass spectra.

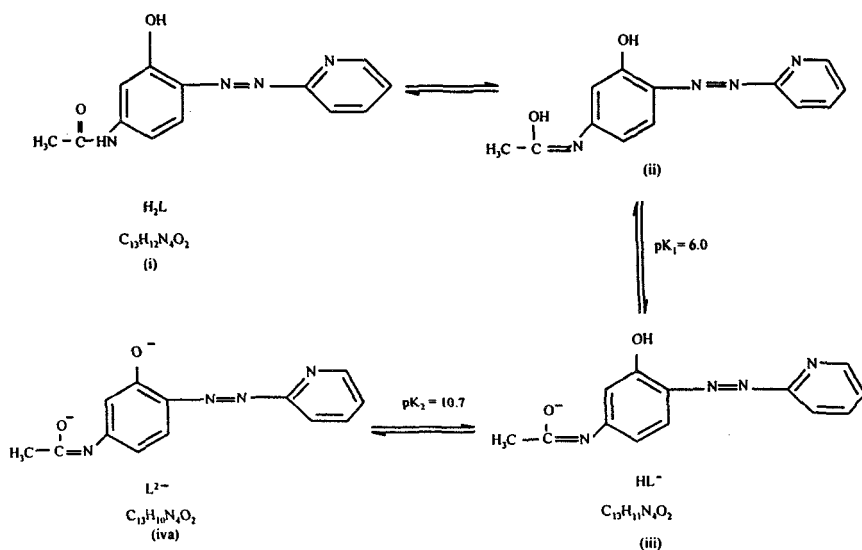
The A_s -pH relation for PAAP ligand is used as a basic principle to determine the pK value spectrophotometrically⁸. It's found that, the PAAP has two pK values, one corresponding to the loss of the acetamide NH proton ($pK_1=1 \times 10^{-6}$), while the second is due to loss of the phenolic OH proton ($K_2=1.99 \times 10^{-11}$) as shown in Scheme (1).

The effect of pH on the PAAP-metal complexes was studied using a universal buffer of different pH values, ranging from 2.0 to 12.0, from which the stability constants of the metal complexes were determined. The values of the stability constants are given in Table (2). It was noticed that, the stability of PAAP metal complexes had the order: Cu (II) > Fe (III) > Ni (II) > Cd (II) > Co (II) > Zn (II).

The Stoichiometry of the complexes was determined by the aid of both molar ratio and continuous variation methods. The results obtained on applying both methods indicate 1:1 metal: ligand complexes.

Metal complexes

As seen from Table (1), the ligand forms 1:1 complexes with the di- and trivalent metals. In order to give sufficient stability to the chelates, the azo group is made part of one or two chelate rings by putting functional groups like phenolic



Scheme (1)

OH group in the ortho positions on the adjacent aromatic groups⁹. The phenolic OH group may lose its proton when coordinated to the Fe (III), Cu (II), Zn (II) and Cd (II) ions, serving to reduce the charge on the complex ion. It may also become coordinated to the metal ion as Co (II) and Ni (II) without the loss of protons, where the charge on the complex ions are neutralized by the presence of chloride ions in the outer sphere of the complexes. Thus 6-(2-pyridylazo)-3-acetamidophenol (PAAP) is expected to fill three coordination positions and contribute a charge of -1 (in the case of the Fe (III), Cu (II), Zn (II) and Cd (II) complexes), or zero as in the Co (II) and Ni (II) complexes. The water solubility of the complexes made calculation of the molar conductivity (Λ_M) of 10^{-3} M solutions at 20°C possible¹⁰, and the type of electrolyte for each complex could be determined (Table 1). The conductance data indicate that Fe (III), Co (II) and Ni (II) complexes are 1:2 electrolyte while Cu (II), Cd (II) and Zn (II) complexes are

TABLE 2
Dissociation constants of the 6-(2-pyridylazo)-3-acetamidophenol and its metal complexes stability constants.

Compound	λ_{max} (nm)		ε L. mol ⁻¹ cm ⁻¹		pK ₋₁	pK ₋₂	Optimum pH	log K
	alc:water (1:1)	Buffer	alc:water (1:1)	Buffer				
Ligand [H ₂ L]	365	365	2900	14830	6.0	10.7	7.07	---
[Fe (C ₁₃ H ₁₁ N ₄ O ₂) (H ₂ O) ₃]Cl ₂	460	375 460	2080	4040 2220	---	---	7.02 9.08	6.043 7.16
[Co(C ₁₃ H ₁₂ N ₄ O ₂) (H ₂ O) ₃]Cl ₂ .4H ₂ O	390	395	3750	4360	---	---	8.02	5.55
[Ni (C ₁₃ H ₁₂ N ₄ O ₂) (H ₂ O) ₃]Cl ₂ .6H ₂ O	375	375	5250	5750	---	---	8.02	5.93
[Cu(C ₁₃ H ₁₁ N ₄ O ₂) (H ₂ O)](OAc).5H ₂ O	375	380	7260	7650	---	---	7.07	7.988
[Zn (C ₁₃ H ₁₁ N ₄ O ₂) (H ₂ O)](OAc).2H ₂ O	375 460	375 460	2536 2410	4040 2280	---	---	8.02 12.2	5.21 8.7
[Cd (C ₁₃ H ₁₁ N ₄ O ₂) (H ₂ O)]Cl. 5H ₂ O	375 460	375 460	3370 2020	3920 2080	---	---	8.02 6.02	5.84 6.98

1:1 electrolytes. This implies the permanence of the initial environment of the metallic ion in the compound obtained and indirect bonding of the ligand to the metal ion.

IR Spectra and mode of bonding

In order to clarify the mode of bonding and the metal ion effect on the ligand, the IR spectra of the free ligand and metal chelates were studied (Table 3) and assigned on the basis of a careful comparison of their spectra with that of the free ligand. The IR spectrum of the ligand reveals a band at 3566 cm^{-1} due to ν (OH). This band is absent in the Cu (II), Zn (II), Cd (II) and Fe (III) complexes, indicating coordination through a deprotonated phenolic OH group¹¹. While in Co (II) and Ni (II) complexes, this band was broadened, decreased in intensity, and shifted to a lower frequency indicating its participation in complex formation via the protonated phenolic OH group. The spectra of the solid complexes exhibits a broad band at $3500\text{--}3400\text{ cm}^{-1}$, which attributed to ν_{OH} of the associated water molecules, while the band observed at approximately $850\text{--}780\text{ cm}^{-1}$ is assigned to coordinated water molecules⁽¹²⁾. This is being supported by the previously reported results⁽¹¹⁾.

The N=N stretching vibrations are shifted to higher frequencies, when the spectra of free ligand is compared with those of its complexes. This result is an indication of the coordination via the azo group in all of the isolated complexes of PAAP ligand. It is hard to specify which of the two nitrogen atoms participate in the chelate ring formation. In the case we have examined, the nitrogen atom adjacent to the hydroxy group is certainly the one which is involved¹¹, otherwise a four-membered chelate ring would be formed. The IR spectrum of the ligand reveals a band at 1322 cm^{-1} due to ν (C-N) of the pyridine ring. This band is absent in all complexes, indicating coordination through the pyridyl nitrogen atom.

In the far IR spectra of all the complexes, the occurrence of bands at $546\text{--}558\text{ cm}^{-1}$ (M-N) and $360\text{--}396\text{ cm}^{-1}$ (M-O) provide evidence regarding the bonding of nitrogen and oxygen to the central metal ion¹⁰.

TABLE 3
Selected IR data (4000-200 cm⁻¹) for 6-(2-pyridylazo)-3-acetamidophenol and its complexes

Compound	ν (N-H)	ν (OH)	ν (C=O)	ν (N=N)	ν (C-O)	ν (C-N)	ν (M-O)	ν (M-N)	ν (M-O) (Coord H ₂ O)
Ligand [H ₂ L]	3398	3566	1699	1522	1266	1321	-----	-----	-----
[Fe (C ₁₃ H ₁₁ N ₄ O ₂) (H ₂ O) ₃]Cl ₂	3213	disap	1558	1517	1292	disap	369	555	863,810
[Co(C ₁₃ H ₁₂ N ₄ O ₂) (H ₂ O) ₃]Cl ₂ ·4H ₂ O	3083	3534	1699	1513	1245	disap	376	558	849
[Ni(C ₁₃ H ₁₂ N ₄ O ₂) (H ₂ O) ₃]Cl ₂ ·6H ₂ O	3162	3545	1710	1509	1256	disap	373	552	859,782
[Cu(C ₁₃ H ₁₁ N ₄ O ₂) (H ₂ O)](OAc)·5H ₂ O	3271	disap	1705	1513	1250	disap	396	554	859,780
[Zn(C ₁₃ H ₁₁ N ₄ O ₂) (H ₂ O)](OAc)·2H ₂ O	3161	disap	1682	1518	1244	disap	375	556	850,780
[Cd (C ₁₃ H ₁₁ N ₄ O ₂) (H ₂ O)]Cl·5H ₂ O	3214	disap	1623	1506	1258	disap	361	546	840

Solid reflectance spectra and magnetic susceptibility measurements

The solid reflectance spectra of the copper complex give bands in the range near 460 nm, which is consistent with tetrahedral or square planar environment¹³. The magnetic susceptibility measurements lie in the 1.85-1.89 $\mu_B/\text{Cu}^{\text{II}}$ range, indicative of antiferromagnetic spin-spin interaction through molecular association. Hence, the copper complex appears to be in square planar geometry with $d_{x^2-y^2}$ ground state¹³. A characteristic band is observed at 364 nm, that is possible due to Cu-Cu interaction¹⁴.

The magnetic moment of Ni (II) complex has been found to be 3.82 B.M. which is within the range of values corresponding to octahedral geometry. The solid reflectance spectra of Ni (II) complex are consistent with the formation of an octahedral geometry with the appearance of three bands at :

$$\nu_1: (5.86-11.07) \times 10^3 \text{ cm}^{-1}: {}^3A_{2g} \rightarrow {}^3T_{2g}$$

$$\nu_2: (11.24-18.87) \times 10^3 \text{ cm}^{-1}: {}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$$

$$\nu_3: (21.83-27.47) \times 10^3 \text{ cm}^{-1}: {}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$$

The 10Dq value lies in the range $5.86-11.07 \times 10^3 \text{ cm}^{-1}$ range confirming the octahedral configuration¹³.

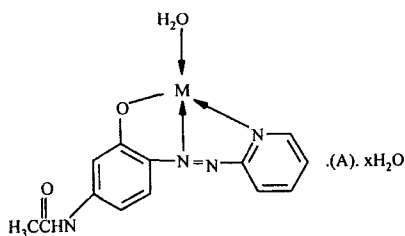
For the cobalt complex, its magnetic moment (5.0 B.M.) is within the range of octahedral cobalt (II) complexes¹⁵. The solid reflectance spectrum shows two bands of medium intensity at 21053 cm^{-1} and 12165 cm^{-1} which assigned respectively to the transition ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ (ν_3) and ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$ (ν_1) of an octahedral cobalt (II) complex. The transition ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) is a two electron process and is normally weak. The ratio ν_3 / ν_1 equals 1.73, which is lower than that expected for octahedral cobalt (II) complexes¹⁶ (1.95-2.48), this indicates a certain amount of distortion from true octahedral geometry due to the presence of a mixed ligand field. The weak band observed at 7179 cm^{-1} is assigned to the spin forbidden ${}^4T_{1g}(\text{F}) \rightarrow {}^4E_g(\text{G})$ transition¹⁷. The Racah interelectronic repulsion parameter for the cobalt complex can be calculated using the following equations¹⁴

$$10 Dq = 2 v_1 - v_3 + 15 B$$

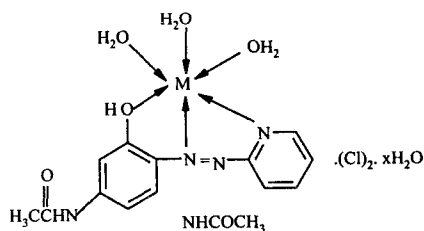
$$B = (1/30) [- (2 v_1 - v_3) \pm (- v_1 + v_3^2 + v_1 v_3)^{1/2}]$$

It is of the order 0.66 of the free ion value, suggesting considerable orbital overlap in the metal σ -bonded¹⁸. The magnetic moment of iron (III) complex has been found to be 4.29 B.M., which is within the range of values corresponding to high spin octahedral complexes of iron (III) ions. Zinc and cadmium complexes are diamagnetic and are likely to be tetrahedral.

On the basis of the above observations, the following structures may be proposed for the above studied complexes:



M : Cu(II), x=5 and A:acetate.
 M: Zn(II), x=2 and A : acetate.
 M: Cd(II), x=5 and A = Chloride.



M : Ni(II), (x=6)
 M: Co(II), (x=4)
 M: Fe(III), x=0

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