Factors of formation of Schiff Compounds

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Abstract:A Schiff base (named after Hugo) is a compound with the general structure $R_2C=NR'$ (R' ≠ H). They can be considered a sub-class of imines, being either secondary ketimines or secondary aldimines depending on their structure. The term is often synonymous with azomethine which refers specifically to secondary aldimines (i.e. R-CH=NR' where R' ≠ H).

A number of special naming systems exist for these compounds. For instance a Schiff base derived from an aniline, where R^3 is a phenyl or a substituted phenyl, can be called an anil, while bis-compounds are often referred to as salen-type compounds.

The term Schiff base is normally applied to these compounds when they are being used as ligands to form coordination complexes with metal ions. Such complexes do occur naturally, for instance in Corrin, but the majority of Schiff bases are artificial and are used to form many important catalysts, such as Jacobsen's catalyst.

Keywords: naphthol , metal .

I.INTRODUCTION

Schiff bases are common enzymatic intermediates where an amine, such as the terminal group of a lysine residue, reversibly reacts with an aldehyde or ketone of a cofactor or substrate. The common enzyme cofactor PLP forms a Schiff base with a lysine residue and is transaldiminated to the substrate(s).[6] Similarly, the cofactor retinal forms a Schiff base in rhodopsins , including human rhodopsin (via Lysine 296), which is key in the photoreception mechanism . An example where the substrate forms a Schiff base to the enzyme is in the fructose 1,6-bisphosphate aldolase catalyzed reaction during glycolysis and in the metabolism of amino acids. Schiff bases can be synthesized from an aliphatic or aromatic amine and a carbonyl compound by nucleophilic addition forming a hemiaminal, followed by a dehydration to generate an imine

II.EXPERIMENTAL

Materials and physical measurements

All chemicals used were of highest purity (BDH or Fluka) and used with out further purification. Elemental analysis was carried out by means of micro analytical unit of (Euroverctor, EA300A,Italy) C.H.N element analyzer .Absorption spectra were recorded using Shimadzu UV-Vis 1700 spectrophotometer, for solution of the complexes in aqueous ethanol at room temperature. Using 1cm quartz cell. IR spectra were recorded with FT-IR-8000 Shimadzu, in the range of (4000-400) cm^{-1} using KBr disc. The magnetic susceptibilities of the complexes were measured on powered samples using the faraday method, for this purpose Balance Magnetic susceptibility model – M.S.B. Auto.Electrical conductivity measured by Digital conductivity meter Alpha – 800 with solute concentration of $10^{-3}M$ in ethanol at room temperature. pH measurements were carried out using (PH– meter), 720 , WTW 82362. ,the metal percentages were determined using atomic absorption technique by Shimadzu -AA-160.

Synthesis and characterization of azo ligand (4-AAP-2-N)

The ligand prepared by dissolving (0.01 mol) of 4-aminoantipyrine in 10 ml of distilled water and 5ml of concentrated hydrochloric acid, then the solution was cooled below 5 °C. To this mixture a solution of (0.01 mol) of sodium nitrate in 10 ml of distilled water was added drop wise at 0-5 °C and the mixture was stirred for 15 min. This diazonium solution was added drop wise to a 500 ml beaker containing (0.01 mol) of 2- Naphthol dissolved in 150 ml of alkaline ethanol. The mixture was allowed to stand over night and acidified with dilute hydrochloric acid to pH = 7.0. The crude dyes were collected by filtration and recystallized from hot Ethanol and then dried in the oven at 60 °C for three hrs. The structural formula of the ligand is shown in figure.1.

Synthesis of complexes

The chelate complexes have been synthesized at optimal pH values dissolved (0.716gm, 0.002 mol) of ligand (4-AAP-2-N)in 10 ml ethanol and then (0.01 mol) of metal chloride, M= Co(II), Ni(II), or Cu(II) dissolved in 10 ml of buffer solution of ammonium acetate (at optimal pH) is added drop wise with vigorous stirring to the ligand solution. The reaction mixture was left over night then the complexes are filtered off washed with distilled water, then with ethanol and dried in desiccators over anhydrous $CaCl_2$. Table.1 collects the physical properties and analytical data for

those complexes are shown in Table 1.
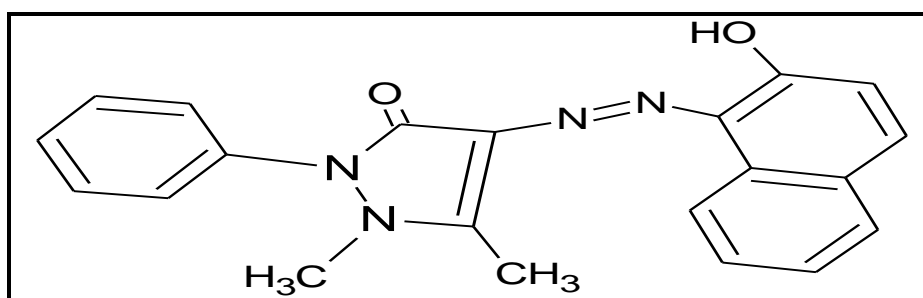
**Figure(1):- Structure of the ligand1-[(4-Antipyril)azo]-2- naphthol (4-AAP-2-N)**

Table(1):- Physical properties and analytical data of the ligand (4AAP-2-N) and its complexes.

No.	Compound	Color	m.p C°	Found . (Calc.)%			
				C	H	N	M
1	$C_{21}H_{18}N_4O2$	Orange	142	70.39 (70.40)	5.02 (4.90)	15.64 (15.38)	—
2	$[Co(C_{21}H_{18}N_4O2\,)_2]$	Red	201	65.03 (65.22)	4.38 (3.98)	14.45 (14.09)	7.60 (7.78)
3	$[Ni\,(C_{21}H_{18}N_4O2\,)_2]$	Dark Red	176	65.05 (64.86)	4.38 (4.22)	14.45 (14.62)	7.57 (7.17)
4	$[Cu\quad(C_{21}H_{18}N_4O2\,)_2].$	Brawn	192	64.65 (64.44)	4.36 (3.95)	14.36 (14.02)	8.15 (8.45)

Results and Discussion
Effect of pH

Suitable pH values for metal complex solutions were found to be in the range of (5 – 10). To evaluate the optimal pH values of metal complex solutions by using buffer solution of ammonium acetate The preparation of the complexes has been conducted after fixing the optimum conditions of concentration which obey Lampert-Beers Law these concentration were (5 x 10^{-4}- 9 x $10^{-4)}$M. The effect of pH on the absorbance were studied, and the results are shown in Figs. 2, 3 and 4.
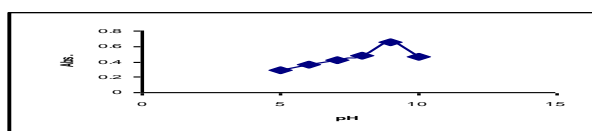
Figure(2):-The effect of pH on the absorbance Of metal complexe Co(II) with the ligand(4-AAP-2-N))at optimal conc. = 9 x 10^{-4} M

Metal: ligand ratios

The metal : ligand ratio (M:L)of complexes were determined by the molar ratio method at the wavelength of maximum absorption (λ_{max}) and fixed PH and concentration .The ligand (4-AAP-2-N)was found to form chelates with all metal ions mention as shown in Figs. 3, 4. The results are in agreement with the values reported for some antipyrilazo   complexes[17,18].

Absorption spectra

The absorption spectra of ligand (4-AAP-2-N) and its complexes were studied and shown in figures 8,9,10 and 11. The wavelength for the maximum absorption (λ_{max}) of the ligand was found at 450nm. The spectra of metal complexes were recorded within wavelength range (497– 503) nm. The absorption maxima (λ_{max}) of each complex also shown in Table.2. .two absorption bands were appear at the free ligand (4-AAP-2-N) spectrum. The bands at 273 nm referring to the $\pi\rightarrow\pi^*$ transitions of Antipyrin ring while the band at 450 nm is due to the charge transfer characters[17].

Table(2):- The optimal pH values, optimal molar concentration and wavelength (λ_{max}) metal ions

Metal Ions	Optimal pH	Optimal molar conc. X 10^{-4} M	Optimal wave length (λ_{max})nm
Co(II)	8	9	497
Ni(II)	9	9	499
Zn(II)	8	9	503

Infrared spectra

The infrared spectra of the free ligand (4AAP-2-N) and its complexes with Co (II),Ni (II)) and Cu(II) are given in Table.3. These spectra are complicated owing to the extensive overlap of number of bands arising from υ(O─H), υ(C═C), υ(C═O), υ(N═N) and other bands due to the Antipyrin and Naphthole rings which appeared in the region below 1700 cm-1. The comparison between the IR spectral data of the free ligand with that of its complexes are discussed as follow:-

1- The spectrum of azo ligand (4AAP-2-N) show absorption band around 1680 cm^{-1}due to the υ(C═0)groups. This suggests that the band due to(C═0)group in Antipyrin ringe[17]. band in each of Co (II),Ni(II) and Cu (II) complexes indicates that this band share in complexation. This band is observed with a little change in shape and shifted to lower frequencies (1608 – 1612) cm^{-1} in complexes. These differences may suggest the linkage of metal ions with oxygen of carbonyl group of heterocyclic Antipyrin ring

2- The spectrum of ligand shows absorption band at 1580 cm^{-1} due to υ(C═C) of Antipyrin and naphthole rings[17-19].This band is observed with a little change in shape and shifted to lower frequencies (1521 – 1570) cm^{-1} in complexes. These differences may suggest the linkage of metal ions with nitrogen of heterocyclic Antipyrin ring[17].

3- The azo group (N═N) appears at 1462 cm^{-1} in the free ligand spectrum. This band has been shifted to different frequencies (1420-1478) cm^{-1} in complexes spectra; this means that some linkage of metal ions with nitrogen atom of azo group takes place[20,21].

4- The spectrum of azo ligand (4AAP-2-N) show absorption band around 3500 cm^{-1}due to the υ(O-H)group. This suggests that the band due to(O-H)group in naphthole ringe[17].band in each of Co (II),Ni(II) and Cu (II) complexes indicates that this band share in complexation. This band is observed with a little change in shape and shifted to lower frequencies (3480 – 3487) cm^{-1} in complexes. These differences may suggest the linkage of metal ions with oxygen of Hydroxide group of heterocyclic naphthole ring

5- Finally a new weak bands appears at (412-432) cm^{-1}in the complexes spectra which may suggest the linkage of metal ions with nitrogen atom[17,21]. The IR spectra indicate that azo naphthole ligand (4AAP-2-N) behaves as a tridentate chelating agent coordinated through nitrogen of azo group and the oxygen of carbonyl group of heterocyclic Antipyrin ring and the oxygen of hydroxide group of naphthole ring.

6- . Figs. 12, 13, 14 and 15 shows the spectra of ligand (4AAP-2-N), and it,s complexes spectra .

Table(3):- Characteristic IR absorption bands of the ligand (4AAP-2-N) and its complexes in cm^{-1} units.

No.	Compound	υ(O─H)	υ(C═0)	υ(C═C)	υ(N═N)	υ(M─N)
1	$C_{21}H_{18}N_4O_2$	3500	1680	1580	. 1462 .	─
2	[Co($C_{21}H_{17}N_4O_2$)$_2$)]	3487.	1610	1570	1478	420
3	[Ni($C_{21}H_{17}N_4O_2$)$_2$]	3480	1608	1521	1421	432
4	[Cu ($C_{21}H_{17}N_4O_2$)$_2$].	3486	1612	1560	1420	412

Magnetic susceptibility and electronic spectra measurements

The magnetic momentum and electronic spectra studies have been used to confirm geometry of the complexes

.These data are listed in Table.4.

Cobalt (II) complex: The value of magnetic moment of Co (II) was found to be 4.52 B.M, which can be a normal value for octahedral [22,23]. The magnetic momentum of the Co (II) complex has been found to be paramagnetic and the high spin behavior of this complex indicates that Co (II) is not oxidized to Co (III) during complexation.. **Nickel (II) complex** :The value of magnetic moment of Ni (II) was found to be 2.85 B.M, which can be a normal value for octahedral Ni (II) complex [24] . **Copper (II) complex :**The magnetic moment value of this complex was found to be 1.68 B.M, suggest the presence of one unpaired electron in this complex. It is reasonable to assign distorted octahedral structure[25]

Conductivity measurements

All complexes show the conductivity measurement values ranging between (8.31 – 13.22) $S.cm^2. mol^{-1}$in DMSO at room temperature, these values indicating nonionic structure of these complexes[7].The conductivity values are listed in table 4.

Table(4):- Conductivity measurements, Magnetic moment of complexes

Complex	Conductivity $S.cm^2.mol^{-1}$	μ_{eff} B.M
$[Co(C_{21}H_{17}N_4O_2)_2$	8.31	4.52
$[Ni(C_{21}H_{17}N_4O_2)_2]$	6.52	2.85
$[Cu (C_{21}H_{17}N_4O_2)_2]$.	13.22	1.68

According to the results the coordination number of all metal ions is found to be six with bonding through the N of azo group and the O of carbonyl group of heterocyclic Antipyrin ring and the O of hydroxide group of naphthole ring. The structural formula of prepared complexes is most probably octahydral
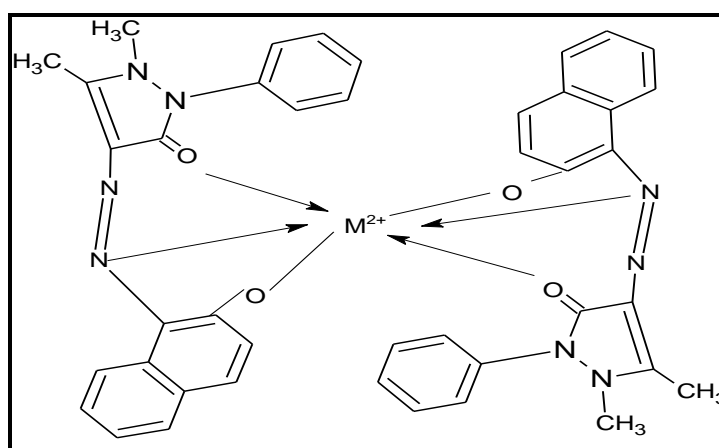
M= Co (II), Ni(II) and Cu (II)
Figure(1):- The proposed structural formula of Co (II), Ni (II)and Cu (II)
Biological Activities of(4-AAP-2-N) and its complexes:
Chemicals on facing the biological system may express multiple effects like, anti bacterial, antifungal, antiviral as well as anti neaplastic effects Besides, they may be inert [26] In the present work the Biological Activities studied using - Mueller – Hinton agar technique

The diameter of the radius of the inhibitory zone reflects the potency of the tested compound.
using -Mueller – Hinton agar technique was applied in the work to measure the bacterial sensitivity of Staphylococcus aureus, pseudomonas aeruginosa to the ligand(4-AAP-2-N) and its complexes of Co(II), Ni(II), and Cu(II) were tested against each of agram positive and gram negative at the concentration $1x10^{-3}$M using ethanol as suitable solvent . the results of antibacterial activities show that all the complexes and the the ligand were active against each of agram positive and gram negative except the complex of Nickel was non active against gram negative (pseudomonas aeruginosa). The size of the inhibition zones were determined of each complex the results shown on table(5)

Table(4):- Inhibition area of the bacterial sensitivity to (4-AAP-2-N) and its complexes

COMPOUND	Inhibition area Staphlococcus aureus (+)	Inhibition area pseudomonas aeruginosa(-)
$C_{21}H_{18}N_4O_2$	++	+
$[Co(C_{21}H_{17}N_4O_2)_2]$	++	+
$[Ni(C_{21}H_{17}N_4O_2)_2]$	+++	-
$[Cu (C_{21}H_{17}N_4O_2)_2]$.	++	+

Not:
(0-6)mm =- (Non active)
(6-9)mm =+ (Slightly active)
(9-12)mm=++ (Moderately active)
(12-17)mm=+++ (Highly active)

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