SYNTHESIS, CHARACTERIZATION AND DETERMINATION OF FORMATION CONSTANTS OF 1, 2 – BIS (2, 5 - DIMETHOXYBENZYLIDENE) HYDRAZINE WITH ZINC (II) AND NICKLE (II) SALTS BY VISIBLE SPECTROPHOTOMETER

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***ABSTRACT**: A novel yellow colored 1, 2 - bis (2, 5 - dimethoxybenzylidene) hydrazine having molecular formula $C_{18}H_{20}N_2O_4$ was synthesized and confirmed by electron impact mass spectrometry and fourier transformed infrared spectroscopy. Yield of the ligand was 91.4% with melting point 172°C whereas λ_{max} was found as 570nm. Formation constants of 1, 2 - bis (2, 5 - dimethoxybenzylidene) hydrazine with $NiCl_2.6H_2O$, $NiSO_4$, $Zn(NO_3)_2.6H_2O$ and $ZnCl_2$ by job's method of continuous variations using visible spectrophotometer were determined as 7.99 [L:Zn (1:1)] for chloride and 7.99 [L:Ni (2:3)] for sulphate which were greater than the values of ligand with $Zn(NO_3)_2.6H_2O$ {6.81 at [L:Zn (1:1)} and then $NiCl_2.6H_2O$ {6.61 [L: Ni (2:1) & (1:1)]} and then {6.00 [L: Zn (2:1)]} with $Zn(NO_3)_2.6H_2O$.*

Key Words: Azine synthesis, Characterization, Formation constants, Spectrophotometer, Job's method

INTRODUCTION

Azines are useful for the isolation, purification, and characterization of carbonyl compounds along with several advantages as protective agents. Azines show extensive biological properties as antibacterial, antifungal, antiviral, anti-inflammatory, antitumor agents, antidepressant, antimalarial and therapeutic agents. These act as binding molecules or modulators of biological receptors making them suitable candidates for drug development [1].

A variety of methods have been employed for synthesis and characterization of azine based complexes. Coumarin azine derivatives have been used as colorimetric chemosensor for Hg^{2+}[2].

In addition to this, a novel heterocyclic azine and its complexes with Ni(II), Co(II), Zn(II) and Fe(III) have been synthesized and analyzed by elemental and spectral analysis [3].

Stability constants of complexes of azine based ligands with rare metals La(III), Pr(III) & Sm(III) in binary solvent dioxane-water mixture have been determined by applying Job's method of continuous variation spectrophotometry [1, 4].

Ligand ratio of complexes formed by spectrophotometric reagent for different complexes can be calculated from the slope ratio, mole ratio method and the Job's method of continuous variation [5].

Reddy *et al* determined the stoichiometry of gallacetophenone phenylhydrazone complexes with metals at 300°C by maintaining the ionic strength constant through Job's method and reported the order of stability constant for the metals as Fe(II) > Ti (IV) > Mo (VI) > Al (III) [6].

Formation constants of complexes have been determined by using RAFA on spectrophotometric data and the stoichiometry of complexation between the Schiff base and Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} cations has been found as 1:1 and for Pd^{2+} as 2:1 [7].

Wolfgang K. studied that the structural consequences of electron transfer as well as the capability for efficient and variable metal-metal bridging render the tetrazines as valuable components of supramoecular materials [8].

A chemosensor molecule based on ferrocene-quinoxaline recognized mercury (II) cations in acetonitrile solution was reported by Zapata *et al* [9].

MATERIAL AND METHODS

All the chemicals of BDH / Merck were used without further purification. Visible Spectrophotometer (BMS VIS-1100), FTIR (Broker tensor 2-Germany) and Mass Spectrometer (JEOL JMS-600H) were employed in this research work.

Synthesis of 1,2-bis(2,5-dimethoxybenzylidene) hydrazine

2, 5 - dimethoxybenzaldehyde (2g) in 20mL ethanol was refluxed for ten minutes at 78°C with a few drops of acetic acid and then 0.1mL of hydrazine hydrate was added and again refluxed for one hour. The reaction mixture was cooled down at room temperature and filtered to get shining yellow crystals which were washed by ethanol and recrystallized.

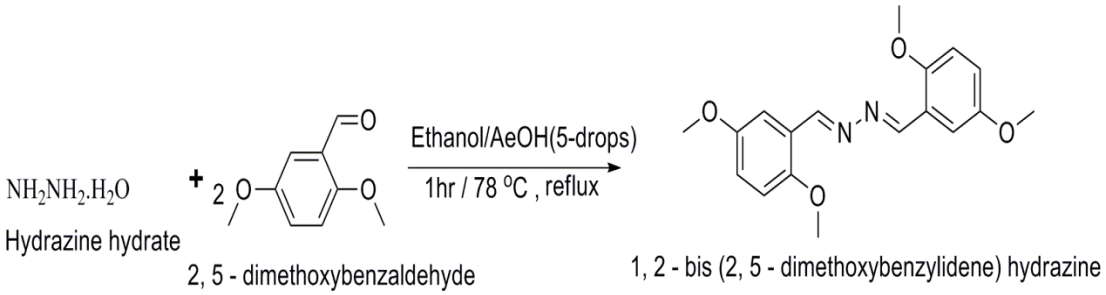
Yield = 91.46%; Color = shining yellow; Melting point = 172°C

DETERMINATION OF FORMATION CONSTANTS

Formation constants of 1,2-bis(2, 5 - dimethoxybenzylidene) hydrazine with zinc (II) and nickel (II) salts such as $ZnCl_2$, $Zn(NO_3)_2.6H_2O$, $NiCl_2.6H_2O$ and $NiSO_4$ were determined by job's method with visible spectrophotometer at λ_{max}570nm. Formation constants were determined by using the following formula:

$$K_f = \frac{\left(\frac{A}{Aex}\right)C'}{\left[\left(Cm-\left(\frac{A}{Aex}\right)C'.\ Cx-\left(\frac{A}{Aex}\right)C'\right)\right]}$$

Where
A = absorbance Peak
A_{ex} = extrapolated absorbance
C' = concentration of complex
C_m = concentration of metal
Cx = concentration of ligand



Scheme: Synthesis of 1, 2 bis (2, 5 - dimethoxybenzylidene) hydrazine

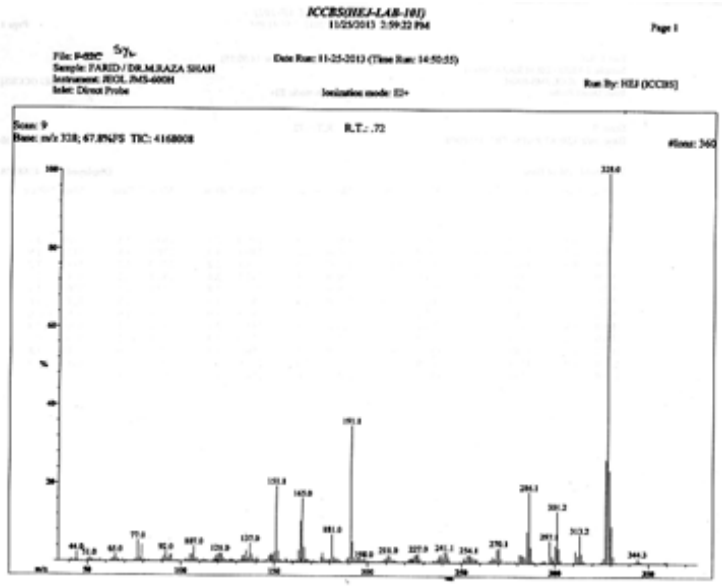


Figure – 1: EIMS OF 1, 2 - bis (2, 5 - dimethoxybenzylidene) hydrazine

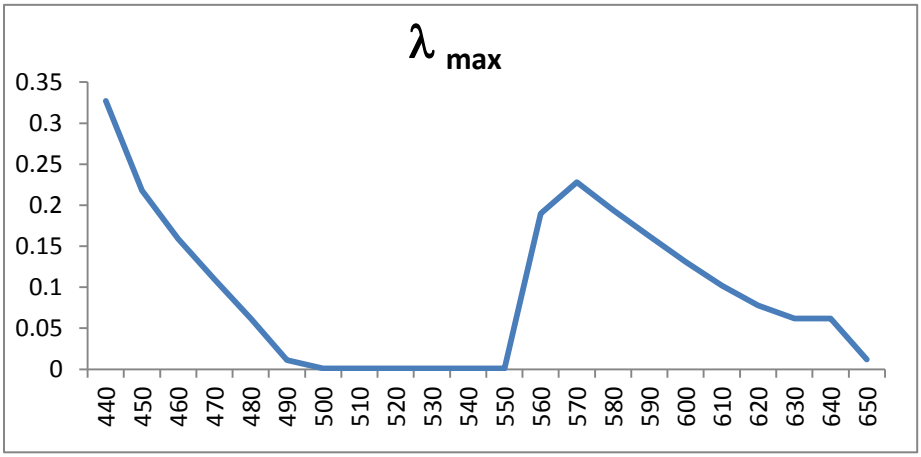


Figure – 2: λ_{max} of 1, 2 - bis (2, 5 - dimethoxybenzylidene) hydrazine

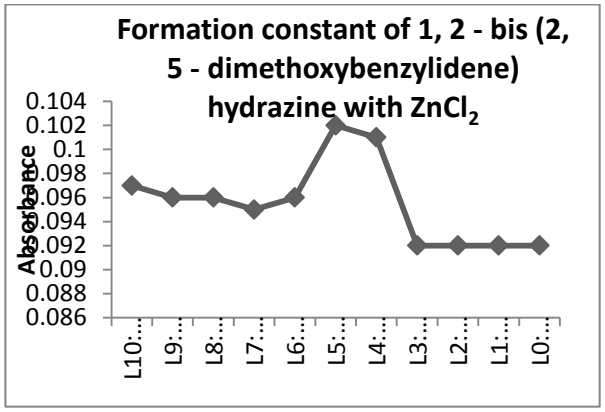


Figure – 3: Formation Constant of 1, 2 - bis (2, 5 - dimethoxybenzylidene) hydrazine with $ZnCl_2$

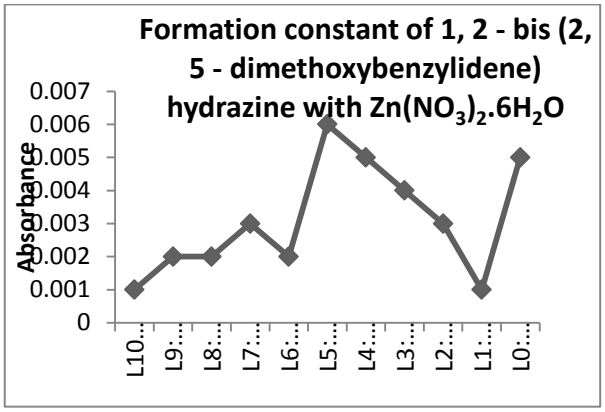


Figure – 4: Formation Constant of 1, 2 - bi's (2, 5 - dimethoxybenzylidene) hydrazine with Zn $(NO_3)_2.6H_2O$

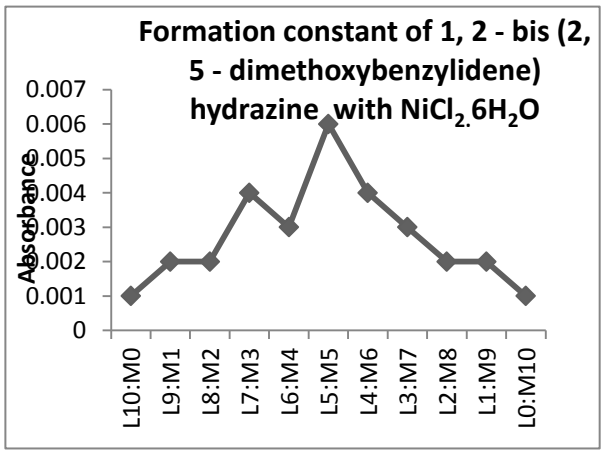


Figure -5: Formation Constant of 1, 2 - bis (2, 5 - dimethoxybenzylidene) hydrazine with $NiCl_2.6H_2O$

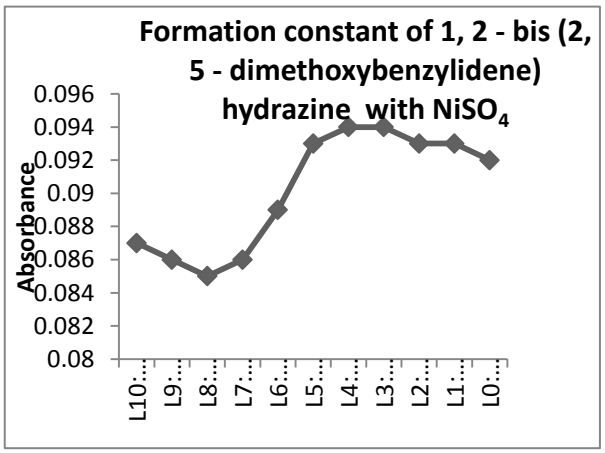


Figure 6: Formation Constant of 1, 2 - bis (2, 5 - dimethoxybenzylidene) hydrazine with $NiSO_4$

Table – 1: Formation Constants of Metal Salts with 1, 2 - bis (2, 5 - dimethoxybenzylidene) hydrazine

S. No.	Metals Salts	Formation Constants		L:M
		K_f	Log K_f	
1	$ZnCl_2$	9.9×10^6	7.99	1:1
2	$Zn(NO_3)_2.6H_2O$	6.5×10^5	6.81	1:1
		1.0×10^5	6.00	2:1
3	$NiCl_2.6H_2O$	4.1×10^5	6.61	2:1
		4.1×10^5	6.61	1:1
4	$NiSO_4$	9.9×10^6	7.99	2:3

Table – 2: FTIR Analysis of 1, 2 - bis (2, 5 - dimethoxybenzylidene) hydrazine

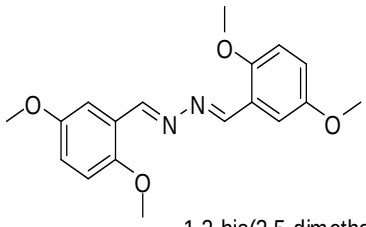
S. No.	Functional group	Frequency (cm^{-1})	
		Spectrum value	Theoretical value
1	Ar C = C	1491.45 (s)	1492
2	OCH_3	1041.38 (s)	1020
3	C = N	1616.5 (m)	1610
4	N - N	1169.82 (m)	1075
5	Ar C - H	2832.28 (w)	2997

RESULTS AND DISCUSSION

1, 2 – bis (2, 5 - dimethoxybenzylidene) hydrazine was synthesized and characterized by FTIR, EIMS (electrton impact mass spectrometer) and visible spectrophotometer. Yellow crystals of 1, 2 – bis (2, 5 - dimethoxybenzylidene) hydrazine were synthesized by the condensation of hydrazine hydrate with 2, 5 -dimethoxybenzaldehyde. The percentage yield was 91.4% and melting point was 172^{o}C.

1, 2 - bis (2, 5 - dimethoxybenzylidene) hydrazine was insoluble in distilled water but soluble in methanol and ethanol.

Molecular mass of 1, 2 - bis (2, 5 - dimethoxybenzylidene) hydrazine having molecular formula $C_{18}H_{20}N_2O_4$ was 328g which was confirmed by Electron Impact Mass Spectrometry (EIMS) and was found nearly equal to the calculated molecular mass.



1,2-bis(2,5-dimethoxybenzylidene)hydrazine

The infrared spectrum of

1,2-bis (2,5-dimethoxybenzylidene) hydrazine was recorded as KBr-disk and main absorption bands are mentioned in table – 3.

FT-IR spectrum recognized five functional groups bands such as aromatic C = C, OCH_3, C = N, N - N and aromatic C - H. Most prominent and strong absorption band was characterized by the absorption arising from the aromatic C = C appeared at 1491.45 cm^{-1}. Another characteristics strong band of OCH_3 was appeared at 1041.38 cm^{-1}. Two medium bands of C = N and N - N were appeared at 1616.5 cm^{-1} and 1169.82 cm^{-1}.

λ_{max} of 1, 2 – bis (2, 5 - dimethoxybenzylidene) hydrazine was 570nm in methanol (Figure - 1).

Job's method of continuous variation was employed for the determination of formation constants of the synthesized 1, 2-bis (2, 5 - dimethoxybenzylidene) hydrazine with transition metal salts such as zinc (II) chloride, zinc (II) nitrate, nickel (II) chloride and nickel (II) sulphate by visible spectrophotometer at λ_{max}570nm.

CONCLUSIONS

It was concluded that values of formation constants of ligand with $ZnCl_2$ and $NiSO_4$ were equal at different stoichiometric ratios (Table – 1, Figures 3 – 6) such as 7.99 [L:Zn (1:1)] and 7.99 [L:Ni (2:3)] which were greater than the values of ligand with $Zn(NO_3)_2.6H_2O$ {6.81 at [L:Zn (1:1)}and then $NiCl_2.6H_2O$ {6.61 [L: Ni (2:1) & (1:1)]} and then $Zn(NO_3)_2.6H_2O$ {6.00 [L: Zn (2:1)]}. The decreasing order of formation constants of 1, 2 –bis (2, 5-dimethoxybenzylidene) hydrazine with transition metal salts was also established.

$ZnCl_2$ = $NiSO_4$ > $Zn(NO_3)_2.6H_2O$ >
7.99 [L: Zn (1:1)] 7.99 [L: Ni (2:3)] 6.81 [L: Zn (1:1)]

$NiCl_2.6H_2O$ > $Zn(NO_3)_2.6H_2O$
6.61 [L: Ni (2:1) & (1:1)] 6.00 [L: Zn (2:1)]

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