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PHYSICO-CHEMICAL AND SPECTROPHOTOMETRIC STUDY OF STABILITY CONSTANT OF Co(II), Ni(II) AND Cu(II) METAL COMPLEXES WITH LIGANDS 3- (2-HYDROXYPHENYL)-1-PHENYL-1H-PYRAZOLE-4-CARBALDEHYDE DERIVATIVES

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ABSTRACT

Co(II), Ni(II) and Cu(II) metal complexes with 3-(2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL¹), 3-(5-chloro-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL²) and 3-(5-bromo-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL³) ligands derived from reaction of 2-hydroxyacetophenone phenyl hydrazone with POCl₃ have been prepared. Elemental analysis, conductance measurements, magnetic moment, infrared, NMR, ESR and electronic spectral studies have all been used to characterise the complexes. The complexes were discovered to exhibit ML₂, square planar shape and stoichiometry (1:2). The stability constants of Co(II), Ni(II) and Cu(II) metal complexes have been examined spectrophotometrically at an absorption maximum of 415nm, 340nm and 610nm at various temperatures.

KEYWORDS

Complexes, Pyrazole, Stability constant, Magnetic moment and Spectrophotometer.

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INTRODUCTON

In 1889, Buchers¹ discovery of the pyrazole, which he got by decarboxylating pyrazole-3, 4, and 5-tricarboxylic acid, was described for the first time. Pyrazole derivatives have been found to have a wide variety of biological action. In the field of medication revelation, pyrazoles have been tremendously used and therefore pyrazole ring constitutes a relevant synthetic target in pharmaceutical industry. The pyrazole derivative celecoxib which is commercially available is used to treat acute pain, painful menstruation, menstrual symptoms and to lessen the amount of colon and rectum polyps for people with familial adenomatous

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polyposis^{2,3}. Tepoxalin is a non-steroidal anti-inflammatory drug that is also a commercially available pyrazole derivative that is permitted for use in veterinary medicine in the United States and the European Union⁴⁻⁶. There are various book chapters^{7,8} and writing reviews⁹⁻¹¹ committed to the combination of pyrazoles and condense pyrazoles. Pyrazole combination includes the cyclocondensation of hydrazine, or hydrazine derivatives, with 1, 3-dicarbonyl compounds is the principal general strategy. While symmetrical 1, 3-dicarbonyl produces a single pyrazole isomer, unsymmetrical-substituted dicarbonyl produces one or both isomers¹². Based on a review of the literature, we provide the synthesis, characterization, and spectrophotometric analysis of the stability constant of Co(II), Ni(II) and Cu(II) metal complexes with 3-(2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde(HL¹), 3-(5-chloro-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL²) and 3-(5-bromo-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL³) ligands at different temperatures.

MATERIAL AND METHODS

All of the synthetics and solvents utilized were of AR grade were acquired from Sisco-chem Industries. The metal salts were bought from commercial sources. The metal content was calculated using established methods¹³. The electronic spectrum investigations of the complexes were performed in DMF solution (10^{-3}) using an Elico SL 159 spectrophotometer in the 200-1000nm range. The HERAEUS C, H, N-O rapid analyzer was used to obtain the ligand and complex elemental analyses data E.S.R measurements were performed on a VARAN E-109 GHz using DPPH as the reference and a 3200 Gauss field. The magnetic susceptibilities were calculated using the Faraday technique using a Model 300 Lewis Coil Force Magnetometer with a one Tesla field strength at room temperature, the instrument was calibrated with Hg [Co (SCN)₄]^{14,15}.

General procedure for the preparation of phenyl hydrazones

Phenyl hydrazine (24mmol) was added to a solution of the relevant 2-hydroxyacetophenone derivatives (24mmol) in 40ml methanol, and refluxed for two hours. The phenyl hydrazone derivatives were crystallised and filtered after cooling the reaction mixture, the yield was 91-94%.

Preparation of 3-aryl-1-phenyl-1H-pyrazole-4-carbaldehyde

The derivatives of 2-hydroxyacetophenone phenylhydrazone (0.01mol) was dissolved in DMF (15ml) and then POCl₃ (0.03mol) was added drop wise at 0°C. After a complete addition of POCl₃, the reaction mixture warmed at room temperature and heated at 60-70°C for 2.5-3h. The reaction was poured onto crushed ice and then neutralized with 10% aqueous NaOH solution. The precipitate was filtered, strongly washed with water and crystallized from ethanol, yielding 84-88%.

Preparation of metal complexes

The preparation of the Co(II), Ni(II) and Cu(II) metal complexes were carried out by adding a hot solution of chloride salts of each Co(II), Ni(II) and Cu(II) metal of (0.951m mole) in absolute ethanol (5ml) to (0.20g, 0.951m mole) of 3-(2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL¹), 3-(5-chloro-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL²) and 3-(5-bromo-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL³) ligands. The mixtures were refluxed for six hours while being stirred, the precipitates were filtered, cleaned with diethyl ether, recrystallized from hot ethanol, and allowed to cool before drying. The physical characteristics of the ligands and metal complexes are displayed in Table No.1.

RESULTS AND DISCUSSION

Elemental studies were used to characterise the produced pyrazoline ligands and their complexes, Infrared, NMR, ESR, Magnetic moment (MM) analysis, electronic spectral research, and conductance measurement. Elemental analysis revealed that all the compounds have stoichiometry

(1:2) ML_2 . The Faraday method¹⁶ was used to ascertain the magnetic moment μ_{eff} of the metal complexes at room temperature. The μ_{eff} values for the complexes Co(II), Ni(II) and Cu(II) metal complexes with 3-(2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL^1), 3-(5-chloro-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL^2) and 3-(5-bromo-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL^3) ligands were 3.2-3.8, diamagnetic and 1.61-1.65 BM respectively, showing that these complexes have square planar shape.

In terms of molar conductivities, the complexes were determined in DMF at room temperature (1×10^{-3} M) using the Johns and Brad Method¹⁷. The complexes' high molar conductance values they demonstrate that they are electrolytic in character. Infrared spectra of the ligands exhibit a extensive medium intensity band in the range $3450-3300\text{cm}^{-1}$ because of phenolic-OH¹⁸, these bands were not seen in complexes Because of coordination through O via phenolic-OH degradation. The complexes' C=N group is allocated to the band in the range $1640-1590\text{cm}^{-1}$, demonstrating that the coordination of metal ions involves nitrogen. The bands caused by the C=N group in complexes are displaced by $30-20\text{cm}^{-1}$ to a lower frequency. The broad medium intensity band in the area of $3450-3300\text{cm}^{-1}$ in the ligands IR spectra of complexes is caused by phenolic-OH¹⁹, these bands were only lightly visible in complexes because of degradation of phenolic-OH in order to coordinate via O.

The electronic spectral study for the ligands and their complexes were carried out, the ligands HL^1 , HL^2 and HL^3 showed aromatic band around 225nm attributed to benzene ring $\pi-\pi^*$ transition, while the band around 345nm are ascribed to the $n-\pi^*$ transition of the non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base²⁰. In the present study, Ni(II) complexes exhibit a medium intensity board band in the region $15800-16500\text{cm}^{-1}$ and this may be regarded as due to the $^1A_{1g} \rightarrow ^1A_{2g}$ transitions. The band due to the M-L charge transfer band. These observations

indicate that the isolated Ni(II) complexes have square-planar configuration. For the Co(II) complexes with these ligands exhibit two bands around 15500cm^{-1} and another broad band near 20000cm^{-1} corresponding to the transitions $^2A_{2g} \rightarrow ^2B_{1g}$ and $^2A_{1g} \rightarrow ^2E_g$ respectively²¹⁻²³, the high intensity band near 20000cm^{-1} may be attributing to spin allowed d-d transitions²⁴ suggest square planar geometry. For all copper complexes showed a broad band with maximum at 412nm due to metal to ligand charge transfer²⁵. The band maxima observed in the present study for copper complexes is at 16120cm^{-1} . These observation suggest that the copper (II) complexes with these ligands are having Square planar geometries. The Schiff bases and corresponding complexes were scanned for ^1H NMR spectra in DMSO- d_6 solvent in the range of 0-15 δ (ppm) down field of TMS. The ^1H NMR spectrum of these ligands HL^1 , HL^2 and HL^3 in DMSO – solvent gave well-resolved multiplets at 7.52 δ -7.83 δ corresponding to aromatic protons. In the complexes these signals were shifted to lower field were observed at 7.28-7.78 δ due to complexation. In ligands and complexes the multiplets observed in the range 7.22-7.48 δ (ppm) due to resolution of aromatic protons. The resolution of azomethine protons at 8.24-8.47 δ (ppm) in ligands but in complexes these signals are shifted to down field. The signals at 12.16 δ (ppm) due to -OH (phenolic) group of ligands are disappeared in complexes due to -OH (phenolic) group is involved in bonding through oxygen with metal ions. The X-band ESR spectrum of the polycrystalline copper(II) complexes has been recorded at room temperature, measurements on homogeneous powder sample give $g_{||}$ and g_{\perp} values only as observed in the case of copper complexes under study. The width and shapes of the absorption lines offer a means of studying the magnetic coupling and extraction within substance²⁶. The $g_{||}$ and g_{\perp} values are calculated according to the procedure indicated by Peisach and Blumberg. In the present investigation, the observed $g_{||}$ value is 2.02, indicate that the complex is covalent in nature $g_{||} > g_{\perp}$. 2.0036, g_{av} it is evident that the unpaired

electron lies predominantly in the $dx^2 - y^2$ orbital of Cu (II) ion, the g values are related by the expression²⁷. Kivelsen and Nieman²⁸⁻³⁰ were presented that the g_{\parallel} is moderately sensitive function of metal ligand covalently. For ionic environment g_{\parallel} is normally 2.4 or larger and for more covalent environment it is less than 2.3. $G = \{(g_{\parallel} - 2) / (g_{\perp} - 2)\}$ which measures the exchange interaction between copper centre in the polycrystalline solid. In the present study, all copper (II) complexes have G values in the range of 2.15-2.17 indicating the exchange interaction of the copper centers. According to Hathaway³⁰ if value of G is greater than four, the exchange interaction is negligible, where as the value of G is less than four, considerable exchange interaction is indicated in the solid complex. Based on the above observations of elemental analysis, IR, electronic spectral data, ¹H NMR spectra, magnetic measurements, conductance measurements, proposed the square planar structure for Co(II), Ni(II) and Cu(II) metal complexes.

The reaction of 3-(2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL¹), 3-(5-chloro-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL²) and 3-(5-bromo-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL³) ligands with Co(II), Ni(II) and Cu(II) metals was investigated at pH 5.0 + 0.05 buffer solutions, at three temperatures, *i.e.* 25, 30, and 35 °C. The absorption spectra of the pyrazoline derivatives as ligands with copper(II) salt formed a dark blue, where as Ni(II), and Co(II) salts form light green and pale brown, water soluble complexes, these complexes gave an absorption peak at 610 nm, 340nm and 415nm (Figure No.2) and was used for the analytical measurements. Under the same condition pure ligands HL¹, HL² and HL³ does not absorb significantly over the investigated wavelength range. Water behaves as a weak field ligand so metal aquo complex acts as a labile complex, which can be easily replaced by ligands HL¹, HL² and HL³ to form a stable complexes ML₂ (λ_{max} = 610nm, 340nm and 415nm for Cu(II), Ni(II) and Co(II) respectively). Metal salt concentration effects on complex formation

with ligands HL¹, HL², and HL³ show that a two-fold mole ratio of reagent is required for maximal complex formation. The colour development was seen immediately and the absorbance stayed the same. Some conformational characteristics of ligands cannot be altered by metal ion binding. The Composition of Complexes and Stability Constant Job's method of equimolar solutions was used to calculate the stoichiometric ratios of HL¹, HL² and HL³ to Cu(II), Ni(II) and Co(II) in the complex^{32,33}. Cu(II), Ni(II), and Co(II) salts from the standard solution (3×10^{-2} M) were pipetted into seven volumetric flasks (0, 1, 2, 3, - - -6ml), and an aliquot of 3×10^{-2} M HL¹, HL², and HL³ (6, 5, 4, - - - 0ml) correspondingly, while maintaining the same mole ratio. Measurements of absorbance were made at 610nm for all the produced compounds, 340nm and 415nm at three temperatures, *i.e.* 25, 30 and 35°C (Table No.1). The curves showed a maximum at a mole fraction $\chi_{metal} = 1$, which denotes the development of complexes with a 2:1 metal to ligand ratio. The study's use of Job's approach corresponds to the following equation:

$$K_f = \frac{[ML]}{[m][L]} \quad A_2/A_1$$

$$K_f = \frac{A_2}{C_M(1 - \frac{A_2}{A_1})}$$

Where, A_1 = absorbance at break point, A_2 = actual absorbance, C_M = concentration of metals, and C_L = concentration of ligands. The mole ratio was used to measure the absorbance method³⁴⁻³⁵ at 638nm at different temperatures with constant Metal (II) concentrations (0 to 1410-4M) and varying ligand concentrations (0 to 1410-4M), all Cu(II) complexes showed a distinct band at a 1:2 mole ratio (Figure No.4). The mole ratio approach is based on the following equation,

$$K_f = \frac{A/\epsilon b}{(C_M - A/\epsilon b) / (C_L - A/\epsilon b)}$$

Where ϵ_b = molar absorptivity constant, and A = absorbance at peak point. Based on the results of the Job's and Mole ratio procedures, the stability constants have been established, and the average Kf value obtained using two distinct approaches is fairly consistent (Table No.6).

Table No.1: Analytical data of the ligands and their complexes

S.No	Ligands/ Complexes	Yield (%)	M.p (°C)	Molar conduct. $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$	Elemental analysis found/(calcd)					
					M	C	H	N	Cl	Br
1	HL ¹ C ₁₆ H ₁₂ N ₂ O ₂	82	110- 112	82.3	-	72.66 (72.72)	4.49 (4.54)	10.54 (10.60)	--	--
2	HL ² C ₁₆ H ₁₁ N ₂ O ₂ Cl	84	115- 116	88.3	-	64.15 (64.10)	3.72 (3.67)	9.40 (9.34)	11.92 (11.85)	--
3	HL ³ C ₁₆ H ₁₁ N ₂ O ₂ Br	75	105- 106	95.2	-	55.84 (55.89)	3.13 (3.20)	8.22 (8.15)	--	(23.26)
4	Co(L ¹) ₂ Co(C ₁₆ H ₁₀ N ₂ O ₂) ₂	55	210- 211	95.8	10.05 (10.10)	65.95 (65.87)	3.36 (3.43)	9.45 (9.49)	--	--
5	Ni(L ¹) ₂ Ni(C ₁₆ H ₁₀ N ₂ O ₂) ₂	57	232- 233	95.2	10.13 (10.07)	65.84 (65.90)	3.46 (3.43)	9.67 (9.61)	--	--
6	Cu(L ¹) ₂ Cu(C ₁₆ H ₁₀ N ₂ O ₂) ₂	62	185- 186	93.9	10.85 (10.80)	65.42 (65.36)	3.45 (3.40)	9.59 (9.53)	--	--
7	Co(L ²) ₂ Co(C ₁₆ H ₉ N ₂ O ₂ Cl) ₂	55	193- 194	97.6	8.93 (8.99)	58.58 (58.63)	2.78 (2.74)	8.49 (8.55)	10.90 (10.84)	--
8	Ni(L ²) ₂ Ni(C ₁₆ H ₉ N ₂ O ₂ Cl) ₂	54	205- 206	89.4	8.90 (8.96)	58.71 (58.65)	2.80 (2.75)	8.50 (8.56)	10.82 (10.85)	
9	Cu(L ²) ₂ Cu(C ₁₆ H ₉ N ₂ O ₂ Cl) ₂	60	192- 193	88.4	9.55 (9.62)	58.29 (58.22)	2.76 (2.72)	8.55 (8.49)	10.82 (10.76)	
10	Co(L ³) ₂ Co(C ₁₆ H ₉ N ₂ O ₂ Br) ₂	56	208- 209	86.7	7.89 (7.95)	51.80 (51.84)	2.50 (2.44)	7.62 (7.56)	--	21.52 (21.57)
11	Ni(L ³) ₂ Ni(C ₁₆ H ₉ N ₂ O ₂ Br) ₂	65	184- 185	92.5	7.89 (7.93)	51.80 (51.86)	2.46 (2.43)	7.63 (7.56)	--	21.64 (21.58)
12	Cu(L ³) ₂ Cu(C ₁₆ H ₉ N ₂ O ₂ Br) ₂	62	196- 197	96.7	8.55 (8.52)	51.48 (51.52)	2.36 (2.41)	7.58 (7.51)	--	21.50 (21.44)

*The values given in the parenthesis are calculated one.

Table No.2: Jobs continues variation method, experimental data of metal (II) complexes with 3-(2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL¹) at different temperature

S.No	[M] (10 ⁻⁴ mol)	[L] (10 ⁻⁴ mol)	χ_M	Absorbance at 415 nm, 340nm and 610nm for Co(II), Ni(II) and Cu(II) respectively with HL ₁								
				25 °C			30 °C			35 °C		
				Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)
1	0	30	0.0	0.033	0.028	0.031	0.043	0.035	0.033	0.032	0.035	0.033
2	5	25	0.14	0.150	0.152	0.155	0.154	0.158	0.149	0.153	0.162	0.159
3	10	20	0.29	0.252	0.249	0.248	0.262	0.259	0.254	0.276	0.252	0.272
4	15	15	0.43	0.362	0.370	0.365	0.343	0.355	0.368	0.358	0.363	0.368
5	20	10	0.57	0.273	0.265	0.270	0.286	0.275	0.282	0.282	0.272	0.269
6	25	5	0.71	0.180	0.175	0.178	0.173	0.179	0.173	0.173	0.164	0.174
7	30	0	1	0.058	0.055	0.056	0.064	0.042	0.039	0.062	0.048	0.045

Table No.3: Jobs continues variation method, experimental data of metal (II) complexes with 3-(5-chloro-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL²) at different temperature

S.No	[M] (10 ⁻⁴ mol)	[L] (10 ⁻⁴ mol)	χ_M	Absorbance at 415 nm, 340nm and 610nm for Co(II), Ni(II) and Cu(II) respectively								
				25 °C			30 °C			35 °C		
				Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)
1	0	30	0.0	0.035	0.026	0.037	0.040	0.036	0.034	0.035	0.032	0.032
2	5	25	0.14	0.152	0.153	0.154	0.156	0.157	0.148	0.156	0.164	0.153
3	10	20	0.29	0.256	0.250	0.249	0.268	0.253	0.253	0.275	0.253	0.278
4	15	15	0.43	0.363	0.373	0.364	0.344	0.358	0.369	0.359	0.367	0.369
5	20	10	0.57	0.275	0.262	0.276	0.287	0.274	0.283	0.283	0.278	0.263
6	25	5	0.71	0.181	0.176	0.177	0.175	0.177	0.174	0.172	0.169	0.172
7	30	0	1	0.057	0.053	0.055	0.059	0.045	0.038	0.052	0.042	0.044

Table No.4: Jobs continues variation method, experimental data of metal (II) complexes with 3-(5-bromo-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL³) at different temperature

S.No	[M] (10 ⁻⁴ mol)	[L] (10 ⁻⁴ mol)	χ_M	Absorbance at 415nm, 340nm and 610nm for Co(II), Ni(II) and Cu(II) respectively								
				25 °C			30 °C			35 °C		
				Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)
1	0	30	0.0	0.036	0.029	0.033	0.035	0.032	0.036	0.039	0.035	0.034
2	5	25	0.14	0.153	0.154	0.154	0.155	0.153	0.148	0.153	0.166	0.152
3	10	20	0.29	0.254	0.252	0.247	0.267	0.258	0.255	0.274	0.258	0.278
4	15	15	0.43	0.368	0.372	0.366	0.349	0.354	0.369	0.359	0.369	0.364
5	20	10	0.57	0.276	0.263	0.273	0.283	0.277	0.283	0.283	0.275	0.263
6	25	5	0.71	0.183	0.173	0.176	0.172	0.176	0.178	0.176	0.169	0.178
7	30	0	1	0.052	0.051	0.053	0.055	0.045	0.040	0.064	0.043	0.045

Table No.5: Representative Mole ratio method, experimental data of Metal (II) complexes with 3- (2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4- carbaldehyde (HL¹) at different temperature

S.No	[M] (10 ⁻⁴ mol)	[L] (10 ⁻⁴ mol)	Absorbance at 415 nm, 340nm and 610nm for Co(II), Ni(II) and Cu(II) respectively								
			25°C			30°C			35°C		
			Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)
1	06	0	0.000	0.000	0.033	0.000	0.000	0.031	0.000	0.000	0.023
2	06	2	0.082	0.088	0.093	0.085	0.086	0.088	0.079	0.078	0.076
3	06	4	0.140	0.148	0.152	0.145	0.155	0.153	0.155	0.145	0.154
4	06	6	0.163	0.173	0.168	0.167	0.165	0.172	0.164	0.168	0.172
5	06	8	0.174	0.178	0.179	0.176	0.175	0.182	0.179	0.175	0.185
6	06	10	0.184	0.186	0.188	0.187	0.186	0.189	0.182	0.184	0.189
7	06	12	0.186	0.196	0.195	0.191	0.193	0.198	0.093	0.192	0.199

Table No.6: Metal-ligand formation constants calculated from Job's continuous variation method and mole ratio method (x10⁴) at 25°C, 30°C and 35°C and P^H of 5.0 ± 0.05

S.No	Methods	M: L	Formation constants (x10 ⁴) at 25°C, 30°C and 35°C temperatures								
			25°C			30°C			35°C		
	Job's		Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)
1	M(L ¹) ₂	1:2	13.2	10.5	11.8	9.33	9.50	8.30	8.40	7.50	6.30
2	M(L ²) ₂	1:2	10.18	9.82	10.3	9.10	8.30	7.32	7.98	6.02	5.65
3	M(L ³) ₂	1:2	9.50	8.9	8.2	8.23	7.36	6.34	7.35	6.00	4.96
Mole ratio			Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)
4	M(L ¹) ₂	1:2	0.45	0.43	0.39	0.36	0.34	0.32	0.33	0.29	0.28
5	M(L ²) ₂	1:2	0.62	0.55	0.56	0.51	0.49	0.41	0.40	0.35	0.33
6	M(L ³) ₂	1:2	0.53	0.43	0.42	0.44	0.39	0.32	0.38	0.27	0.22

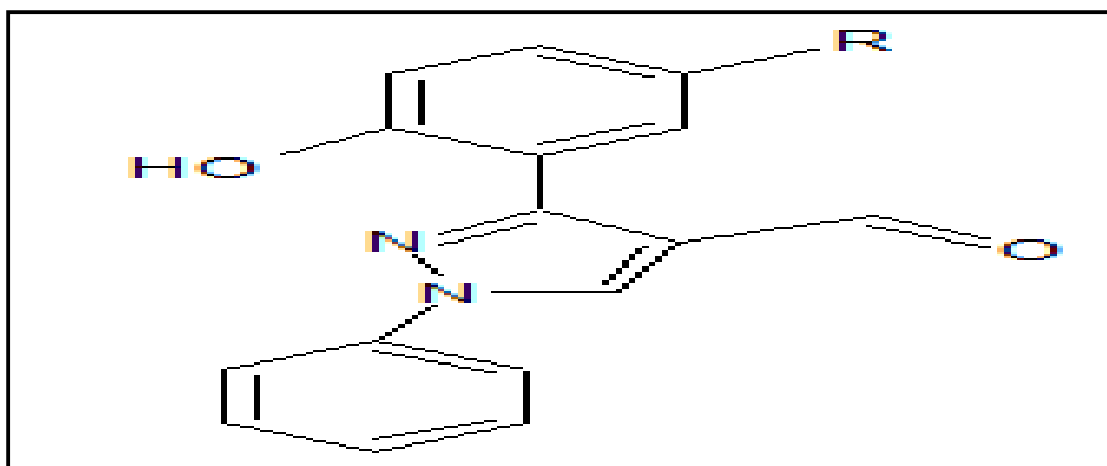


Figure No.1: HL¹ = 3-(2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde
R= H, Cl and Br

HL² = 3-(5- chloro-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde

HL³ = 3-(5-bromo-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde

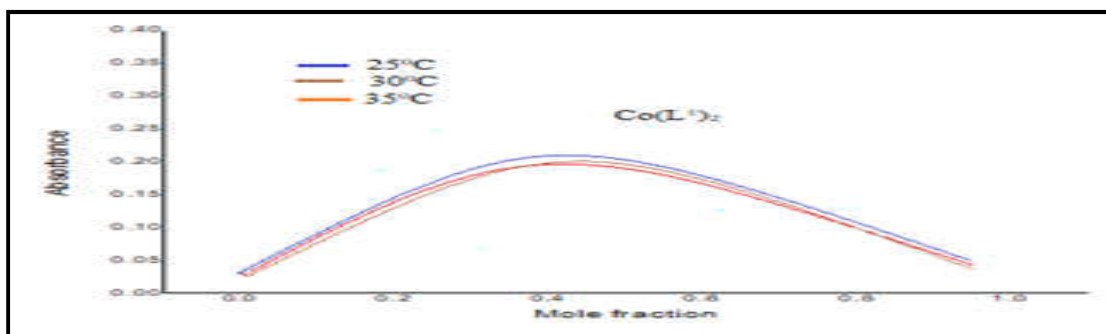


Figure No.2: Representative Jobs curve for $\text{Co(L}^1\text{)}_2$ complexes at various temperature

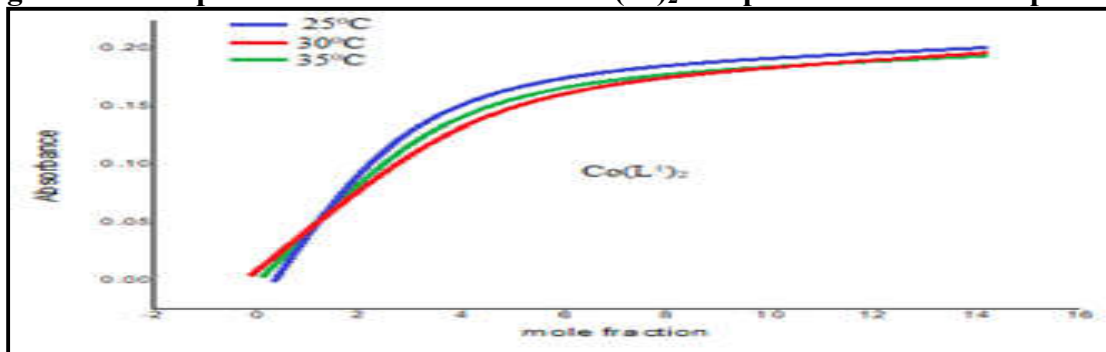


Figure No.3: Representative Mole ratio curves for $\text{Co(L}^1\text{)}_2$ complexes at various temperature

CONCLUSION

This paper mentioned that, the creation and evaluation of novel bidentate ligands, specifically: 3-(2-Hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL^1), 3-(5-Chloro-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL^2) and 3-(5-Bromo-2-hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (HL^3) and their Co(II), Ni(II) and Cu(II) metals complexes. The analytical results indicated that all complexes should have a 1:2(M:L) stoichiometry. The prepared compounds are electrolytic in medium. Based on the IR measurements and electronic spectrum data mentioned above, ^1H NMR spectra, magnetic, conductance measurements, proposed the square planar structure for Co(II), Ni(II) and Cu(II) complexes. The stability constant information from Job's approach corresponds well with the equivalent numbers from the mole ratio method by spectrophotometric method. Complexes are formed in an acidic media at room temperature. It has been noted that the complexes formation constant lowers with rising temperature.

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CONFLICT OF INTEREST

We declare that we have no conflict of Interest.

BIBLIOGRAPHY

1. Wiley R H. The Chemistry of heterocyclic chemistry: Pyrazoles, pyrazolines, pyrazolidines, indazoles and condensed ring; Behr, L C; Fusco R; Jarboe C H; *Interscience Publishers, John Wiley and Sons*, 1967, 3-20.
2. Habeeb A G, Rao P N P, Knaus E E. Design and synthesis of celecoxib and rofecoxib analogues as selective cyclooxygenase-2 (cox-2) inhibitors: Replacement of sulfonamide and methylsulfonyl pharmacophores by an azido bioisostere, *Journal of Medicinal Chemistry*, 44(18), 2001, 3039-3042.

3. Szabo G, Fischer J, Kis-Varga A, Gyires K. New celecoxib derivatives as anti-inflammatory agents, *J. Med. Chem*, 51(1), 2008, 142-147.
4. Leone S, Ottani A, Bertolini A. Dual acting anti-inflammatory drugs, *Curr. Topics Med. Chem*, 7(3), 2007, 265-275.
5. Zhou I, Ritchie D, Wang E Y, Barbone A G, Argentieri D, Lau C Y. Tepoxalin, a novel immunosuppressive agent with a different mechanism of action from cyclosporin A, *J. Immunology*, 153(11), 1994, 5026-5037.
6. Lee D H S, Macintyre J P, Taylor G R. Tepoxalin enhances the activity of an antioxidant, pyrrolidine dithiocarbamate, in attenuating tumor necrosis factor α -induced apoptosis in WEHI 164 cells, *JPET*, 289(3), 1999, 1465-1471.
7. Eicher T, Hauptmann D, Speicher A. The chemistry of heterocycles, *Ed.; Wiley VCH: Federal Republic of Germany*, 2nd Edition, 2003, 86-184.
8. Gilchrist T I. Heterocyclic chemistry, *Addison Wesley, Longmann: Harlow*, 3rd Edition, 1992, 432.
9. Makino K, Kim H S, Kurasawa Y. Synthesis of pyrazoles and condensed pyrazoles, *J. Heterocycl. Chem*, 36(2), 1999, 321-332.
10. Escribano F C, Alcantara M P G. Heterocycle formation from 1, 3- dinitroalkanes, A novel pyrazole synthesis, *Tetrahedron Lett*, 29(46), 1988, 6001-6004.
11. Grimmett M R, Iddon B. Synthesis and reactions of lithiated monocyclic azoles containing two or more hetero-atoms, Part III: Pyrazoles, *Heterocycles*, 37(3), 1994, 2087-2147.
12. Gupton J T, Clough S C, Miller R B, Norwood B K. The application of vinylogous iminium salt derivatives to the regiocontrolled preparation of heterocyclic appended pyrazoles, *Tetrahedron*, 58(27), 2002, 5467-5474.
13. Vogel A I. A Text book of quantitative inorganic chemistry, *ELBS and Longmanns Green and Co. Ltd. London*, 3rd Edition, 1962.
14. Setwood P W. Magneto chemistry, *Interscience, New York*, 2nd Edition, 1958.
15. Jain A C, Mathur S K, Shashadri T R. *J. Sci. Ind. Res*, 21B, 1962, 214.
16. Berezovskii V M, Yurkevich A M. An improved synthesis of adenine, *Zh. Obshch. Khim*, 32, 1962, 1655-1659. *Ref. Chem. Abstr*, 58, 1963, 4566d.
17. Sayed H H, Aymne Rashad. Synthesis and biological evaluation of some pyrimidine, pyrimido [2, 1-b] [1, 3] thiazine and thiazolo [3, 2-a] pyrimidine derivatives, *Acta Pharm*, 56(2), 2006, 231-244.
18. Curtis N F. Transition-metal complexes with aliphatic schiff bases, Part I. Nickel (II) complexes with N-isopropylidene-ethylenediamine schiff bases, *J. Chem. Soc*, 10, 1960, 4409-4413.
19. Kohout J, Smogrovic J K. Copper (II) complexes with organic ligands, VII. Magnetic properties of copper (II) acetate and copper (II) salicylate complexes of pyridine and quinoline N-oxides, *Chemické Zvesti*, 22(7), 1968, 481-492.
20. Nakamoto N. Infrared and raman spectra of inorg and coord, Complexes, *John Wiley, New York*, 3rd Edition, 1978.
21. Nishida Y, Kida S. *Bull. Chem. Soc. Japan*, 45, 461(1961).
22. Lever A B P. Inorganic Electronic spectroscopy, *Amsterdam, Elsevier*, 1960.
23. Nishikania H, Yamada S. *Bull. Chem. Soc, Japan*, 13(8), 1964.
24. Gray H B. *Trans. Met. Chem*, 1, 1965, 240.
25. Bailer J C, Emeleus J H T, Nyholm R S, Dikenses A F T. *Pergamon Press, Oxford*, 1973.
26. Nishida Y, Kida S. Magnetic moments and electronic spectra of low-spin cobalt (II) complexes, *Bull. Chem. Soc. Japan*, 45(2), 1972, 461-465.
27. Usharani M. Derivation of N, N, O donor sites of organic schiff base ligand based on 2-hydroxynapthalene-1-carbaldehyde and their cu (II) and co (II) complexes, *Int. J. Advanced Sci Tech Res*, 5(3), 2013, 198-206.

28. Lancanster F W, Walter Gordy. Paramagnetic resonance absorption of microwaves, *J. Chem. Phys*, 19(9), 1957, 1181.
29. Hirianaya K. Choudhry, Okhil K. Medhi. Spectroscopic studies on imidazole adducts of iron(III)quadridentate schiff base complexes, *Ind J. Chem*, 37A(2), 1988, 130-135.
30. Kivelsen O, Neiman R. ESR studies on the bonding in copper complexes, *J. Chem. Phys*, 35(1), 1961, 149-155.
31. Hathaway B J and Billing D E. The electronic properties and stereochemistry of mono-nuclear complexes of the copper (II) ion, *Coord. Chem. Rev*, 5(2), 1970, 143-207.
32. Likussar W, Boltz D F. Theory of continuous variations plots and a new method for spectrophotometric determination of extraction and formation constants, *Anal Chem*, 43(10), 1971, 1265-1272.
33. Das A R and Nair V S K. A spectrophotometric determination of the second dissociation constant of 5-nitrosalicylic acid and the stability of its 1:1 copper complex in aqueous solution at 25°C, *J Inorg Nucl Chem*, 34(4), 1972, 1271-1275.
34. Tarun Kumar Pal, Md. Ashraful Alam, Subrata Paul, Md. Chanmiya Sheikh, Hasan Ahmad. Physico-chemical, antioxidant and antimicrobial investigation on new mixed ligand complexes containing bis (2, 4, 4-trimethylpentyl) dithiophosphinic acid and 2, 2'-bipyridine, *Oriental Journal of Chemistry*, 34(3), 2018, 1213-1221.
35. Harvey A E, Manning D L. Spectrophotometric methods of establishing empirical formulas of colored complexes in solution, *J Am Chem Soc*, 72(10), 1950, 4488-4493.

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