

Research Article

Mixed Ligand Complexes of Diamino Pyrimidine Azo Dyes with some Transition Metals and Glycine, DL- Alanine or Glutamic Acids

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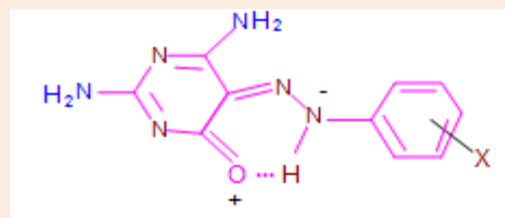
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Abstract

The overall formation constants of ternary complexes of Cu(II), Co(II), Ni(II) with Glycine (Gly), DL- Alanine (Ala) and Glutamic Acids (Glu) as primary and 5-(arylamino)2,6-diamino-4-pyrimidinol as secondary ligands as well as those of the binary systems have been investigated potentiometrically in 40 % (v/v) EtOH-H₂O at 25 °C and I=0.15 M NaClO₄. The stability of the ternary complexes is quantitatively compared with that of the corresponding binary complexes. The data were interpreted on the basis of statistical considerations and the nature of complexes. The concentration distribution of various species formed in solution was evaluated.

Keywords: Mixed ligand, Diamino Pyrimidine, Azo Dyes, Amino Acids.

The Cu(II), Co(II) and Ni(II) complexes have been synthesized and the coordination sites of the ligands were characterized by means of IR and ¹HNMR spectroscopy.

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Introduction

It is suggested that the ternary complexes have been implicated in storage and transport of active substances through biological membranes. Also, the use of arylazo heterocyclic N donor ligands to stabilize low oxidation states like Cu(II) and Co(II) is widely studied in coordination chemistry [1-4]. These phenomena were dependent upon the chelate stability and the nature of involved metal ion [5-7]. Mixed complexes of transition metals containing a pyrimidines group as ligands are commonly found in biological media and have important roles in processes as catalysis of drugs interaction with biomolecules [8-12]. These types of compounds have been shown to be versatile ligands for preparation of polymolecular complexes which coordinates in a bi-, tri- and tetradentate fashion [13,14]. Further interest in these families of compounds arises from their existence in aqueous media as protonated, neutral and deprotonated species. Each of these prototropic species can act differently with metal ion yield neutral complexes with different composition stability and photo-redox properties [15-16].

We report, here, the results of pH-metric studies of Cu(II), Co(II) and Ni(II) complexes containing glycine (Gly), DL-alanine (Ala) and glutamic acid (Glu) as primary ligands and 5-(4-N,N-diethyl-1-phenylazo)-2,6-diamino-4-pyrimidinol (L₁); 5-(1-naphylazo)-2,6-diamino-4-pyrimidinol (L₂); 5-(4,N,N-nitro-1-phenylazo)-2,6-diamino-4-pyrimidinol (L₃); and (4-N,N-1-phenylazo)-2,6-diamino-4-pyrimidinol (L₄) as secondary ligands. The work aims to establish the various equilibria existing and the stability constant of binary and ternary complexes in 40 % (v/v) EtOH-H₂O at 25°C and I = 0.15 M NaClO₄.

Experimental**Materials and Reagents**

All the chemicals used in the preparation of the azo dyes were A.R. products from BDH and Merck. The azo compounds 5-(4-N,N-diethyl-1-phenylazo)-2,6 diamino- 4-pyrimidinol (L_1); 5-(1-naphylazo)2,6 diamino- 4-pyrimidinol (L_2); 5-(4,N,N-nitro-1-phenylazo)- 2,6 diamino- 4-pyrimidinol (L_3); and (4-N,N-1-phenylazo)- 2,6 diamino- 4-pyrimidinol (L_4) were synthesized by the procedure as described by Vogel [17]. Ligand stock solutions were prepared by dissolving the calculated amount in in 40% (v/v) EtOH- H_2O mixture and were standardized by pH- titration with standard $HClO_4$. Solutions of the metal ions Cu(II), Co(II) and Ni(II) were prepared in doubly – distilled water and metal content was determined by complexometric EDTA titration [18]. pH measurements were carried out on a MV 87 digital pH –messgerate accurate to ± 0.005 unit equipped with a glass electrode and saturated calomel electrode. The following mixtures (total volume of 50 ml) were titrated against CO_2 –free 0.1 M NaOH, $HClO_4$ (a); a + amine (b) ; b + metal ion (c); a + azody (d); d + metal ion (e), and a + amine + azodye + metal ion (f). The ionic strength was adjusted to 0.15 mol dm^{-3} by addition of $NaClO_4$ as supporting electrolyte . The pH meter reading (β) recorded in 40% (v/v) EtOH- H_2O solutions were converted to $[H^+]$ by means of relation of Van Uitert and Hass [19].

The absorption spectra in the UV and visible were recorded on a Shimadzu UV-1650 PC , UV-Visible Recording Spectrophotometer using 1 cm matched silica cell. The IR spectra have been recorded with a perkin-Elmer 983B IR recording spectrophotometer. The 1H NMR spectra were recorded with a varian Em-390 spectrometer at 90 MHz in DMSO. TMS were used as internal reference.

Results and Discussion

Proton-Ligand Systems

The proton binding and metal binding constants of the different species are detected from the potentiometric, pH titrations of the free and complexed ligands over the pH range 2.0-12.0. The obtained curves are represented graphically in Figs (1-3).

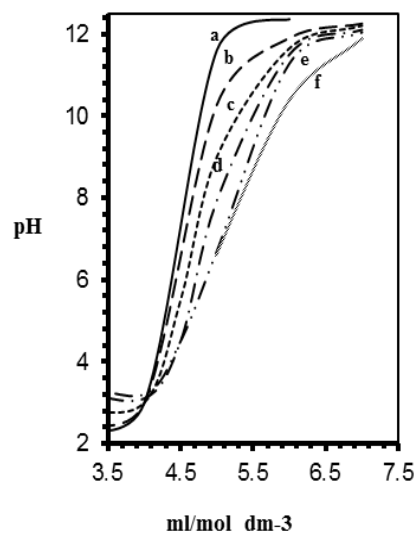


Figure 1 Titration curves for the Cu(II)-Glu-L2 system at $25^\circ C$ and $\mu = 40\% \text{ EtOH}$
 a) 0.01 HClO_4 , (B) solution (a) $+ 3.0 \times 10^{-5} \text{ Glu}$, (c) solution (b) $+ 1.5 \times 10^{-5} \text{ Cu(II)}$
 (d) solution (a) $+ 3.0 \times 10^{-5} \text{ L}_2$, (e) solution (d) $+ 1.5 \times 10^{-5} \text{ Cu(II)}$, (f)
 (f) solution (e) $+ 3.0 \times 10^{-5} \text{ Glu}$, concentration of NaOH 0.1 mol dm^{-3} .

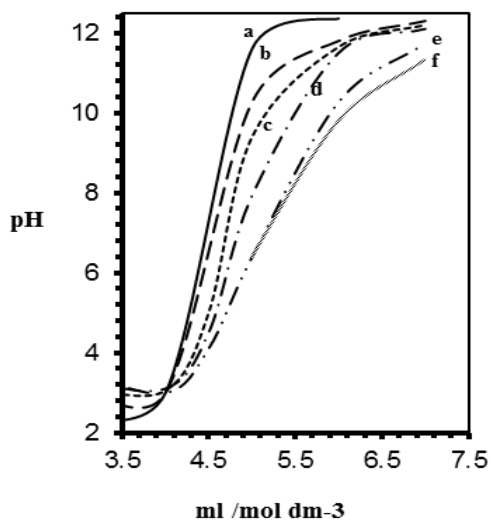


Figure 2 Titration curves for the Co(II)-Glu-L2 system at 25^o C and $\mu = 0.15$ and 40% EtOH, (a) 0.01 HClO₄, (B) solution (a) + 3.0×10^{-5} Gly, (c) solution (b) + 1.5×10^{-5} Co(II), (d) solution (a) + 3.0×10^{-5} L2, (e) solution (d) + 1.5×10^{-5} Co(II), (f) solution (e) + 3.0×10^{-5} Gly, concentration of NaOH 0.1 mol dm⁻³

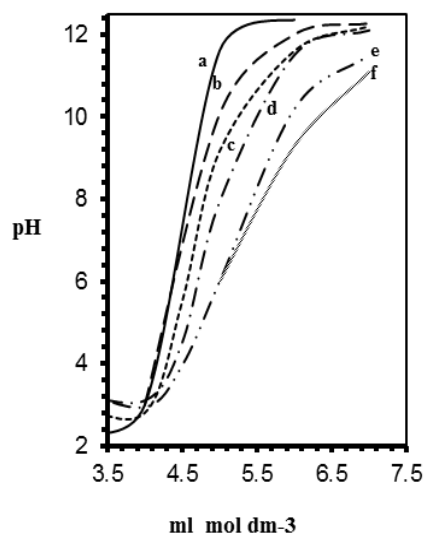


Figure 3 Titration curves for the Ni(II)-Ala-L2 system at 25^o C and $\mu = 0.15$ and 40% EtOH (a) 0.01 HClO₄, (B) solution (a) + 3.0×10^{-5} Ala, (c) solution (b) + 1.5×10^{-5} Ni(II), (d) solution (a) + 3.0×10^{-5} L2, (e) solution (d) + 1.5×10^{-5} Ni(II), (f), solution (e) + 3.0×10^{-5} Ala, concentration of NaOH 0.1 mol dm⁻³

Similar titration features are obtained with other systems. The prototropic behaviour of the free ligands under investigations can be ascribed from the examination of the curves (d), which show two illdefined inflections at (m) values of 1.0 and 2.0 before and after the perchloric acid titration curve (a) respectively (where m denotes the number of equivalents of OH⁻ ions added per mole of ligand present in solution mixture). The first inflection point located in the pH range 3.1-3.96 corresponding to the protonation of NH₂ or hetero nitrogen atoms of the pyrimidine ring. The second inflection appears after the acid curve (a) at pH range 4.2-11.3 is suggested to be due to the dissociation of the enolic hydroxy group of the pyrimidine moiety. This is supported by the fact that the azoaminopyrimidine can be tautomerised to produce amino-ketone and imino-enol forms [20]. The average number of protons bound to the ligand (\bar{n}_A) at various pH values are calculated using the curves (a) and (b), and then the dissociation constants (pK_H) are determined from the plot of \bar{n}_A vs. pH, using the computer program based on the Irving-Rossotti equations [21]. The dissociation constants of glycine, DL-alanin and glutamic acid are also redetermined under the same of our experimental conditions. It is worth mentioning that the first dissociation constant (pK_H) values for the amino acids studied are very low values (~2.3)[22] and exist only in strongly acidic solutions and accordingly these values are not used in calculations. As expected, the amino nitrogen of DL-alanin is a little more basic than with glycine as a result of the inductive effect of methyl group. The pK values obtained through the refinement of several sets of potentiometric data are quoted in Table (1).

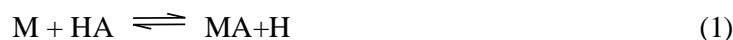
Table 1 Ionisation Constants of The Free Ligands and Stability Constants of binary systems at 25°C, $\mu = 0.075$ M (NaClO₄), (error limit = 0.02-0.06) in log units

Ligands→ Constants ↓	L ₁ (x = p- N(C ₂ H ₅) ₂)	L ₂ (Ar = naphthyl)	L ₃ (x = p-NO ₃)	L ₄ (x = -H)	Gly	Ala	Glu
H ⁺							
log β ₁	5.40	5.95	4.80	5.30	–	–	–
log β ₂	16.35	15.60	13.30	15.63	9.75	9.86	9.65
Cu ²⁺							
log β ₁	6.06	5.86	5.84	6.04	7.90	7.73	7.50
log β ₂	11.61	11.19	11.15	11.58	14.30	14.18	13.70
Co ²⁺							
log β ₁	5.30	5.31	5.12	5.20	6.39	6.10	5.91
log β ₂	9.88	9.35	9.40	9.54	11.70	11.4	11.01
Ni ²⁺							
log β ₁	5.90	5.66	5.60	5.83	6.81	6.70	6.35
log β ₂	10.83	10.06	10.24	10.75	12.84	12.33	11.8

Metal-Ligand Binary Systems

Analysis of the complexed ligands (c) and(d) Figs (1-3) indicates that the addition of metal ion to the free ligand solutions shifts the buffer region of the ligand to lower pH values. Thus shows that complexation reaction proceeds by releasing protons from such ligands. It is observed that MA titration curve (c) diverges from the free ligand curve in the lower pH (~3.5) than ML complex (e) which begins to form at pH ≥ 4.2. In the formed species, there is no precipitation during the titration up to pH 9.8 ruling out the possibility of hydrolysis of the complexes. The complexes are quite stable up at high pH values. The present study shows two weak inflections below the amino acid curve in

case of MA species and a single step inflection during the formation of ML species after addition of two moles of NaOH solution per mole of ligand. This indicates the formation of 1:1 and 1:2 complex species through the liberation of two protons from the free ligand in stepwise manner (A) or simultaneously (L). The probable stepwise complexation equilibria involved in the formation of binary system can be represented by the below equations, (charges are omitted for the sake of clarity).



$$\log K_{MA}^M = \log [MA] - (\log [M] + \log [A]) \quad (2)$$



$$\log K_{MA_2}^M = \log [MA_2] - (\log [MA] + \log [A]) \quad (4)$$

Similarly, for the azo ligands (L) complexes,

$$\log K_{ML}^M = \log [ML] - (\log [M] + \log [L]) \quad (5)$$

$$\log K_{ML_2}^M = \log [ML_2] - (\log [ML] + \log [L]) \quad (6)$$

The overall stability constant can be represented as follows

$$\log \beta^{MA_2} = \log K_{MA}^M + \log K_{MA_2}^M \quad (7)$$

$\log \beta^{MA_2}$ values are initially determined from the titration curves as described earlier [20]. The average number of ligand molecules is attached per metal ion \bar{n} and the free ligand exponent pL using the curves of the ligand in absence and in presence of metal ion. The maximum \bar{n} values obtained are in the range 0.2-1.7 confirming the formation of 1:1 and 1:2 species. The formation curves of the metal complexation equilibria are obtained from the \bar{n} vs. pL plots Figure (4, 5).

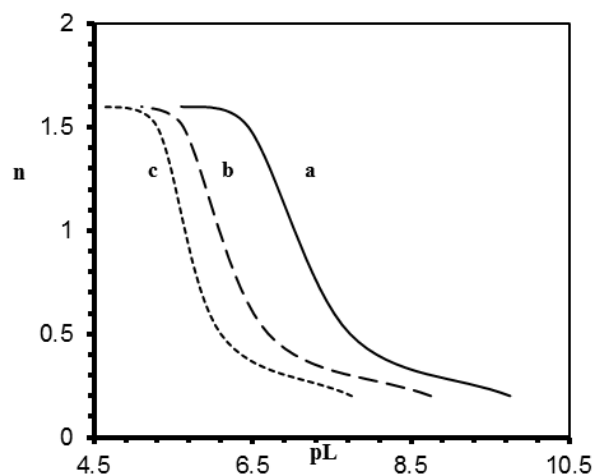


Figure 4 Formation curves for metal ion –Gly binary system

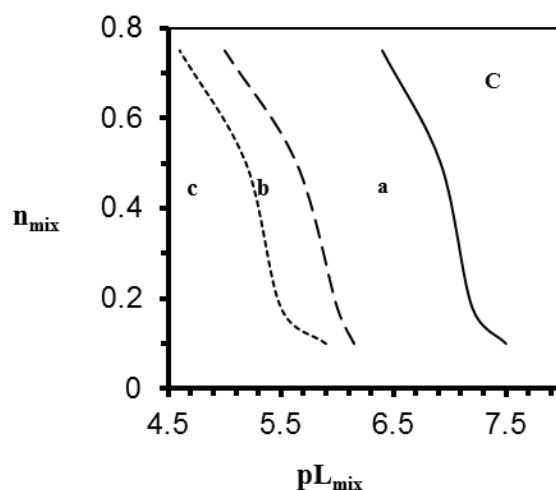
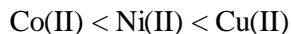


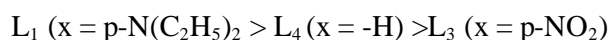
Figure 5 Formation curves for metal ion –Gly binary system

From these plots, the values of overall stability constants $\log \beta_{MA}$ and $\log \beta_{MA_2}$ are determined using half integral method. The obtained values agree well with those obtained from the linear plots of $\log \frac{\bar{n}}{1-\bar{n}}$ vs. pL , where $\log \beta_{MA} = \log [L] = pL$ at $\log \frac{\bar{n}}{1-\bar{n}} = 0$.

The stability constant of $\log \beta$ values for the formed complexes is in accordance with Irving [21] listed in Table (2), which indicates that the formation of 1:1 and 1:2 complex species. The present results show the stability of binary chelates increase in the order :



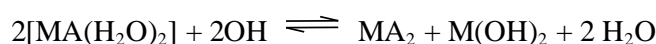
This is in agreement with the general order of stability of Transition metal [21] and can be explained similarly. In terms of the nature of ligand, the stability order of binary system (ML) decrease in the order:



According to that agreements, the more basic ligand can form, the more stable complex is found [23,24]. With respect to the amino acid complexes (MA), the order of stabilities has been found to be Gly > Ala > Glu. This behaviour is in line with the previous reported order [25,26], which does not follow the basicity order of studied amino acids probably due to the similarity in the dissociation constant values of these acids. Therefore, the revisal in the relative order of the stabilities of Gly and Ala complexes can be explained based on the size of substituent, considering that the studied amino acids are derivatives of glycine [27]. Thus, the observed higher stabilities Gly complexes compared to those of Ala complexes may be due to the steric hindrance results from substituent of bulky methyl group on carbon atom bearing NH_2 group. It is suggested that lengthening of alkyl chain in Glu is responsible to lower stability of its complex. Moreover, a comparison of stabilities in terms of the nature of ligand reveals that MA complexes are more stable than the corresponding ML chelates. This behaviour may be explained on the basis that in binary MA complexes, the amino acid acts as monobasic bidentate ligands through the NH_2 nitrogen and $COOH$ oxygen atoms, forming stable five-membered ring. In binary ML complexes, the azopyrimidine ligands coordinate in a mono deprotonated bidentate fashion, through the $N=N$ group of nitrogen and either exocyclic N (6) and O (4) atoms of the pyrimidine moiety forming six membered chelate ring. Therefore, in the transition of metal complexes, the higher stability of MA than ML complexes can be explained based on the fact that the five-membered chelates are more stable than those of six-membered one [28].

Metal-Ligand Ternary Systems

Mixed ligand titration curve of Cu(II)-A-L obtained according the sequence described in experimental section and the Similar titration curves were obtained for Co(II) and Ni(II) is given in Fig (1-3). The shape of the titration curves suggested that the amino acids (A) act as primary ligands during the formation of MAL systems as binary MA (curve, c) is found at lower pH values than those of ML system (curve, e). Examination of the obtained titration curves shows that the curve of ternary systems (curve, f) are located above individual curves of binary MA and ML systems, at low pH values and then superimposed with ML curves and consequently moved below ML curve at pH range 5.2-7.5 which confirms the formation of ternary complex species in solution. Further evidence for the formation of mixed ligand MAL chelates is provide by the presence of an inflection point at $m = 2$, followed by a buffer region in the range of experimental pH values between $m = 2$ and $m = 3$ ($m =$ number of alkali moles added per mole of metal ion). At $\text{pH} \leq 7.5$, the solution mixture of ternary complexes is quite stable and remains clear. This may be due to the redistribution of the electron density of metal-ligand bond in MAL chelates in such a way that these chelates are more polarity than binary chelates and hence, are not hydrolyzed up to pH 7.5, precipitation is observed in some systems due to the hydrolysis of metal ion according to the following reaction:



The interfering effects of hydroxo species are negligible in the range of experimental pH values. Thus, the secondary ligand must be combined with binary chelates solution in similar manner of its interaction with equated metal ion $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ solutions. Further, the observed overlapping of MAL curve (f) at low pH values then runs below MA curves to reveal that the secondary ligand (L) does not participate in ternary complex formation below pH ~ 5.2 . This indicates that the formation of MAL species starts after the formation of MA species. The overall stability constants are calculated, considering that the ternary chelates may be formed simultaneous or in step wise manner according to the following complexation equilibria,

$$\text{M} + \text{A} + \text{L}, \log \beta_{\text{MAL}}^{\text{M}} = \log [\text{MAL}] - \log [\text{M}] + \log [\text{A}] + \log [\text{L}] \quad (8)$$

Since, $\log [\text{M}] + \log [\text{A}] = \log [\text{MA}] - \log K_{\text{MA}}^{\text{M}}$ (Equation 2)

$$\therefore \log \beta_{\text{MAL}}^{\text{M}} = \log [\text{MAL}] - \log [\text{MA}] + \log K_{\text{MA}}^{\text{M}} + \log [\text{L}] \quad (9)$$

Similarly,

$$\text{MA} + \text{L} \rightleftharpoons \text{MAL}; \log K_{\text{MAL}}^{\text{MA}} = \log [\text{MAL}] - (\log [\text{MA}] + \log [\text{L}]) \quad (10)$$

$$\text{ML} + \text{A} \rightleftharpoons \text{MLA}; \log K_{\text{MLA}}^{\text{ML}} = \log [\text{MLA}] - (\log [\text{ML}] + \log [\text{A}]) \quad (11)$$

The overall stability constant of ternary chelates is determined from the following relations;

$$\log \beta_{\text{MAL}}^{\text{M}} - \log K_{\text{MA}}^{\text{M}} = \log K_{\text{MAL}}^{\text{MA}} \quad (12)$$

$$\log \beta_{\text{MLA}}^{\text{M}} - \log K_{\text{ML}}^{\text{M}} = \log K_{\text{MLA}}^{\text{ML}} \quad (13)$$

The horizontal distance between the MA curves (c) and MAL ones (f) are used for calculation of the average number of secondary ligand moles associated with one mole of binary complex, \bar{n}_{mix} and free secondary ligand exponent, pL_{mix} using method described earlier [29]. Then, the initial formation constants of ternary systems are evaluated from the \bar{n}_{mix} vs. pL_{mix} curves as represented in Figure (6).

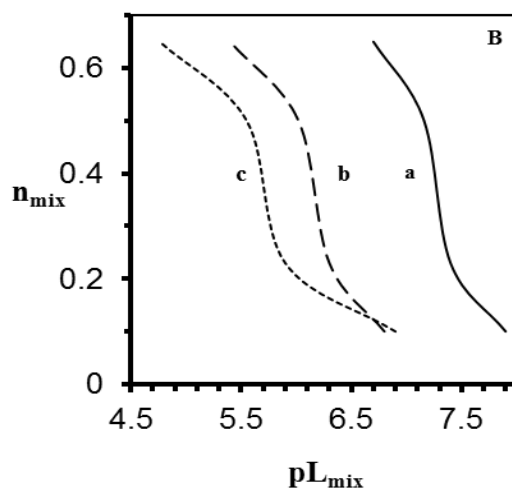


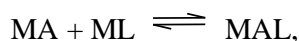
Figure 6 Formation curves for metal ion (a) Cu(II), (b) Co(II), (c) Ni(II)-L₂- Glu , ternary system

Table 2 Stability Constants of M²⁺-Amino acid-Azo Dye Ternary Systems at 25°C

Metal ion	$\log \beta_{MAB}^M$	$\log K_{MAB}^{MA}$	$\log K_{MBA}^{MB}$	$-\Delta \log K_M$	$\log X$	$\Delta \log X'$	$\log \beta_{stat}$
M ²⁺ -Gly-L ₁							
Cu(II)	13.25	5.35	7.24	0.66	0.64	0.84	13.23
Co(II)	11.09	4.80	5.79	0.50	0.60	0.38	11.09
Ni(II)	12.13	5.40	6.23	0.50	0.59	0.22	12.14
M ²⁺ -Gly-L ₂							
Cu(II)	13.05	5.15	7.19	0.71	0.61	0.79	13.04
Co(II)	10.85	4.56	5.65	0.64	0.65	0.24	10.82
Ni(II)	11.81	5.08	6.15	0.58	0.72	0.20	11.75
M ²⁺ -Gly-L ₃							
Cu(II)	13.04	5.14	7.31	0.59	0.74	0.91	12.97
Co(II)	10.89	4.61	5.78	0.51	0.70	0.37	10.85
Ni(II)	11.79	5.08	6.21	0.52	0.54	0.21	11.84
M ²⁺ -Gly-L ₄							
Cu(II)	13.12	5.22	7.22	0.68	0.50	0.82	13.17
Co(II)	10.90	4.60	5.69	0.60	0.54	0.28	10.92
Ni(II)	12.11	5.30	6.28	0.53	0.55	0.23	12.13
M ²⁺ -Ala-L ₁							
Cu(II)	13.24	5.51	7.23	0.50	0.74	0.78	13.17
Co(II)	10.89	4.79	5.59	0.51	0.50	0.29	10.94
Ni(II)	11.92	5.22	6.02	0.68	0.68	0.39	11.88
M ²⁺ -Ala-L ₂							
Cu(II)	13.01	5.28	7.15	0.58	0.65	0.70	12.99

Co(II)	10.63	4.53	5.43	0.67	0.51	0.13	10.67
Ni(II)	11.56	4.86	5.90	0.80	0.73	0.27	11.49
M ²⁺ -Ala-L ₃							
Cu(II)	12.89	5.16	7.16	0.57	0.56	0.71	12.91
Co(II)	10.67	4.57	5.55	0.55	0.54	0.25	10.70
Ni(II)	11.62	4.92	6.02	0.68	0.67	0.39	11.59
M ²⁺ -Ala-L ₄							
Cu(II)	13.10	5.37	7.20	0.53	0.58	0.75	13.11
Co(II)	10.73	4.63	5.53	0.57	0.52	0.23	10.77
Ni(II)	11.80	5.10	5.97	0.73	0.52	0.34	11.84
M ²⁺ -Glu-L ₁							
Cu(II)	12.97	5.47	6.96	0.54	0.68	0.76	12.93
Co(II)	10.71	4.80	5.41	0.50	0.53	0.31	10.75
Ni(II)	11.68	5.33	5.78	0.57	0.73	0.33	11.62
M ²⁺ -Glu-L ₂							
Cu(II)	12.78	5.28	6.92	0.58	0.67	0.72	12.75
Co(II)	10.49	4.48	5.19	0.66	0.54	0.20	10.51
Ni(II)	11.30	4.95	5.64	0.71	0.74	0.21	11.23
M ²⁺ -Glu-L ₃							
Cu(II)	12.72	5.22	6.99	0.51	0.70	0.79	12.67
Co(II)	10.45	4.54	5.33	0.54	0.57	0.27	10.48
Ni(II)	11.26	4.91	5.66	0.65	0.56	0.25	11.28
M ²⁺ -Glu-L ₄							
Cu(II)	12.86	5.36	6.96	0.54	0.58	0.76	12.87
Co(II)	10.56	4.65	5.36	0.55	0.57	0.26	10.57
Ni(II)	11.64	5.29	5.81	0.54	0.73	0.36	11.58

The obtained high values of $\log \beta^{MAL}$ confirm the assumption that the amino acids used act as primary ligands and the formation of ternary complexes is favored by equilibrium (equation 12). In the present study, the behaviour of amino acids is similar to those observed previously [30]. However, in contradiction to those reported by other authors [31], the results show that the stability of ternary chelates follows the same order of the ionic potential of metal as shown in binary systems. It is clear that the stability of ternary systems is always greater than the corresponding binary systems. This data can be interpreted by assuming the σ -donor tendency of amino acid and π -interaction. Hence, due to the accepting character of the pyrimidine moiety, the back donation of π -electrons of d-orbital of metal to antibonding π^* orbital of pyrimidine ring will result in an increase in the positive charge and the electrophilic character of the metal in ternary systems. This leads to a slight increase in $M \rightarrow L$ σ -bonding of the azo ligand compared to $M \rightarrow L$ σ -bond of binary systems [32]. The relative stability constants of ternary complexes are conveniently characterized by comparing the difference instabilities of binary and ternary systems, $\Delta \log K$ [33,34]. These values are calculated from the reaction of secondary ligand (L) either with MA (equation 10) or with the free metal ion (equation 5) and hence, $\Delta \log K = \log K_{MAL}^{MA} - \log K_{ML}^M$. The overall equilibrium can be represented from the following equation,



Hence,

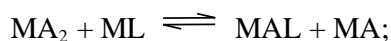
$$\Delta \log KM = \log \beta_{MAL} - (\log K_{MA} + \log K_{ML}) \quad (14)$$

It is found that, in case of binary chelates the $\Delta \log K = (\log K_{ML_2}^M - \log K_{ML}^M)$ values are generally negative as expected, since $K_{ML}^M > K_{ML_2}^M$. This indicates the formation of less stable 1:2 species, which may be due to the coulombic repulsion between the two similar ligands bound to the same metal ion. The $\Delta \log KM$ for the ternary complexes should also be negative, generally in -0.5 to 2.0 range depending on the geometry of the complexes [35]. The negative $\Delta \log KM$ values will result from the presence of a fewer number of binding sites on MA complex than on aquatic metal ion. Thus, it is expected that the secondary ligand bind the MA with small stability. However, the obtained $\Delta \log KM$ for all ternary systems is less negative values shown in **Table 2** which are in contrary to the statistical expectation [32]. This behaviour shows higher stability for ternary chelates (equation 14) compared to binary ones. Based on the suggestion that the $\Delta \log KM$ values depend on the coordination number of the metal ion and the nature of the ligand [36], the change in $\Delta \log KM$ values obtained may be attributed to the change in the geometry of the formed chelates. The less negative values of $\Delta \log KM$ may also be due to the absence of coulombic repulsion between the two dissimilar ligands in the ternary complexes. The data show that $\Delta \log KM$ values of M-Gly-L₃ are more positive than the values obtained for M-Ala-L₂. The marked stability of M-Gly-L₃ may be due to the interligand stacking interaction possibly H-bond formation between the two types of ligands [37], whereas the DI-alanin can not take part in interligand staking [38]. However, the difference between $\Delta \log KM$ values are small indicating that ternary complexes may exist in staked-open intramolecular equilibrium in solution as postulated by Sigel and coworkers [39]. Another parameter generally used to indicate the quantitative stability of ternary complexes compared to the binary one, is based on the disproportionate constants, X, which calculated from the reaction [39,40].



$$\log X = 2 \log \beta_{MAL}^M - (\log K_{MA_2}^M + \log \beta_{ML_2}^M) \quad (15)$$

The values of $\log X$ expected on statistical grounds is +0.6 [40] for all geometry. More positive values than those were expected to indicate marked stability of ternary complexes formed through equation (15). On the other hand, meanwhile the $\log X$ values can indicate the tendency of secondary ligand (L) to coordinate with MA complex, it fail to discuss the effect of ternary complex formation in weakening or strengthen M-A bond. Thus, other stabilization constant ($\log X'$) is considered based on the following equation,



$$\log X' = (\log \beta_{MAL}^M + \log K_{MA}^M) - (\log \beta_{MA_2}^M + \log K_{ML}^M) \quad (16)$$

The observed slight variation in values of each parameter suggested similar mode of binding of the ligands in their complexes. The values of $\log X$ are found to be in the range of the statistical value or more, show that the binary MA₂ complex is less stable than the corresponding tendency complexes. The data, also, shows that the $\Delta \log X'$ values are higher than the order expected on statistical ground (0.2), indicating that the MA and ML bonds in ternary complexes are stronger than those in the binary complexes. This may be explained based on the back donation of metal ion π -electrons to the π -electrons cloud of the secondary azo ligand (L), resulting in strengthening the M→L σ -bond and weakening the M→A one. Further, it is found that the stabilization of MA bond in ternary system increased as the size of amino acids and metal ion decreased. This indicates that the magnitude of $\Delta \log X'$ is marked influenced by steric difference in both ligands and metal ions used. The overall stabilities can be calculated on the basis of statistical ground [41-43] from the following equation,

$$\log \beta_{stat} = \log 2 + 1/2 (\log \beta_{MA_2}^M + \log \beta_{ML_2}^M) \quad (17)$$

The results reported in Table (2) show that the difference between stabilities measured experimentally, $\log \beta_{MAL}$ and calculated by statistical method $\log \beta_{stat}$ are small positive values, confirming that MAL complexes are more

stable than both MA_2 and ML_2 complexes. The high stability of ternary chelates is related to the redistribution of charges over the complexes, which are originated from transfer electrons from ligand orbital (L^-) to the positive MA^+ species leading to the formation of neutral MAL . Thus, the $M \rightarrow L$ σ -covalent bond is increased.

Distribution Diagrams

The distribution profiles of the various azopyrimidine (L) species and free amino acids (A), formed through the change of the pH values of their solutions, are obtained from the plots of pH values of the ligand solution as function of the calculated concentration percentage (α %) of each ligand species using the Pk_a values of these ligands. Typical species-distribution graphs are represented in Figure (7, 8).

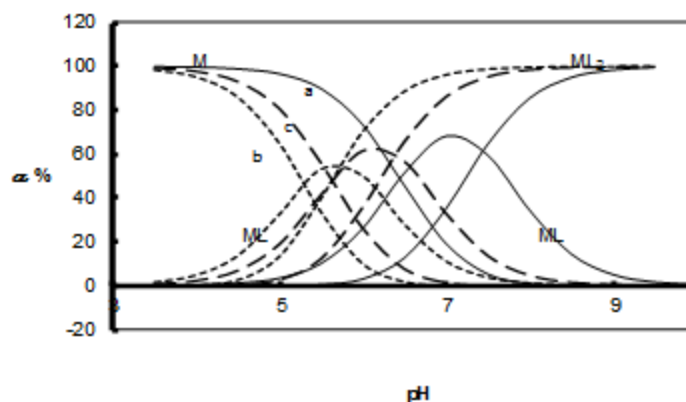


Figure 7 Distribution diagrams of Ala complexes for (a) Cu(II), (b) Co(II) and (c) Ni(II) species

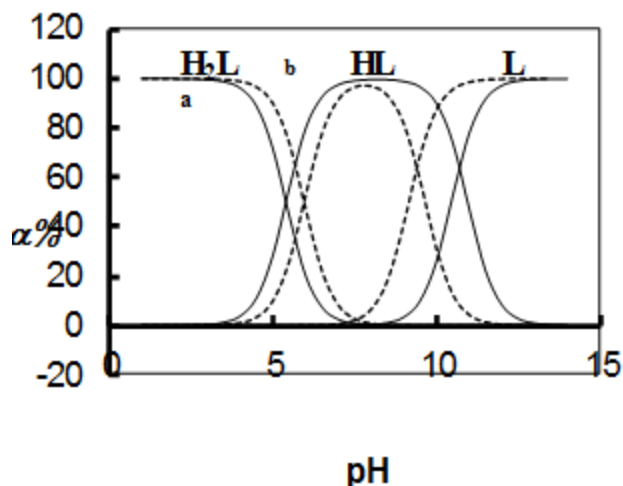


Figure 8 Distribution Diagrams of Ligands L_5 ($x=p-N(C_2H_5)_2$) and L_6 ($R = \text{naphthyl}$) species

As shown from these curves, almost of the free ligand species are present as dissociated species H_2L^+ ($\alpha_{H_2L^+} \approx 99.8$ %) at $pH \leq 2.5$. On increasing the pH of the medium, H_2L^+ species tends to decrease in its concentration, while that $[HL]$ begins to develop. In the pH range 6.0-7.2, the $[HL]$ species reaches maximum concentration of $\alpha_{HL} \approx 90$ %, while that of $[L^-]$ tends to appear. At $pH \approx 5.2$ (L_1, L_3) and $pH = 5.8$, equal concentration of H_2L^+ and HL species are

observed ($\alpha_{HL} = \alpha_{HL} = 49.3\%$). Increasing the pH above 6.0 the α_{HL} decrease and $[L^-]$ species begin to appear. At $pH \approx 8.8$, the HL and L- species are present in equilibrium. The $[L^-]$ species reaches a maximum concentration ($\alpha_{L^-} \approx 97.5\%$) in the pH range 8.8-12.0. At this range the [HL] species almost disappear ($\alpha_{HL} \approx 3.2\%$). For binary systems graphs shown in Fig. (9), the obtained curves are generally showing that, in presence of low concentration of the ligand, [L], all the metal ions will be present as free ions ($\alpha_M \approx 98.7\%$). On increasing [L], the metal ion concentration [M] will begin to decrease while that of [ML] species tends to increase. When the $[L] = 1/K_{ML}$ value, the α_M and α_{ML} will become equal. On increasing [L] above $1/K_{ML}$ value, the [ML] will exceed that of [M]

because the reaction will shift toward [ML] formation. However the values of K_{ML} and K_{ML_2} are so little different that there will be a small value of $[ML_2]$ presence even in solution of [L] equal $1/K_{ML}$ value. On further increasing [L] above $1/K_{ML}$ value, the $[ML_2]$ species as well as [ML] species, increase. The [ML] and $[ML_2]$ species have the

same $\alpha\%$ value at $[L] = 1/K_{ML}$. Increasing [L] than $1/K_{ML_2}$ value, the solution contains more $[ML_2]$ than [ML] species. At high concentration of the ligand, the metal ions is completely disappeared ($\alpha \approx 0.01\%$) and [ML] has low value ($\alpha^{ML} \approx 7.8\%$), while the $[ML_2]$ species 0.02 predominate ($\alpha^{ML_2} \approx 92.2\%$). Species-distribution diagrams of (a) Cu-Gly- L_1 and (b) Cu-Ala- L_4 ternary systems are shown in Figs (9) as representative.

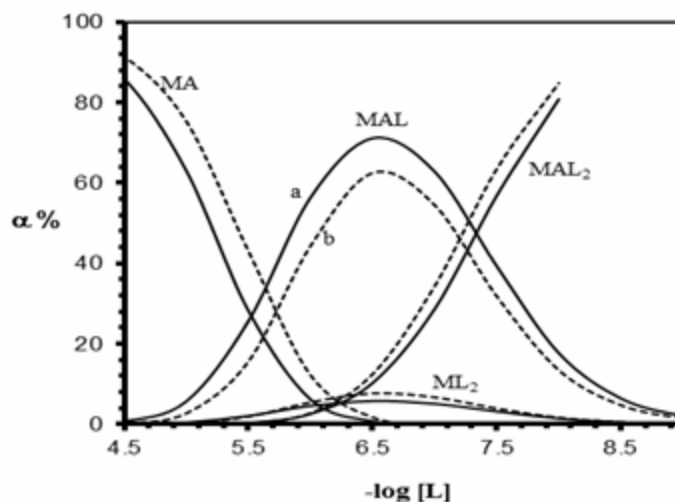


Figure 9 Distribution Diagrams of (a)Cu(II)-Gly- L_5 ,(b)Cu(II)-Ala- L_8 ,ternary system

Similar feature is observed for other ternary systems. The profiles showed that the total concentration of Cu(II) ions in the form of ternary complex species exist in higher concentration than that Ni(II) and Co(II) ions in there corresponding ternary systems, but Cu(II) never exceed 50 % as expected from statistical consideration [34].It is worth mentioning that the obtained graphs are not independent from the initial concentrations of the ligands, since increasing the concentration of one ligand with respect to another may enhance the formation of some species which are not present under different concentration conditions. The best computer models showed the presence of two ternary species of type MAL and MAL_2 , in addition to the various binary species which may result from the reaction, $2MAL \rightleftharpoons MA_2 + ML_2$. Generally, the represented plots indicate that in the presence of lower concentration of [L]than the reciprocal of the formation constants of MA ($1/K_{MAL}$), nearly all Cu(II) ions present as MA complexes ($\alpha_{MA} \approx 83.5\%$, $\alpha_{MA} \approx 88.3\%$ for Cu-Gly- L_1 and Cu-Ala- L_4 respectively). On increasing, the [L], the [MA] decreases while the [MAL] species increase, and these two concentrations have the same value at $[L] \approx 1/K_{MAL}$. On a further increase in [L], the [MAL] will exceed that of [MA], in addition to presence of small concentration of ML_2 chelate ($\alpha(a) \approx 5.2\%$, $\alpha(b) \approx 6.5\%$). At high concentration of [L], the [MAL] reaches maximum ($\alpha(a) \approx 74.0\%$, $\alpha(b)$

$\approx 59.5\%$) and $\alpha_{ML_2} = 7.1\%$, while $[MA]$ almost disappeared ($\alpha_{MA} \approx 1\%$). In these concentrations, $[MAL_2]$ begin to increase ($\alpha_{ML_2} \approx 18.6\%$). At $[L]$ more than $1/\beta_{MAL}$ value, the $[MAL_2]$ tends to increase at the expense of $[MAL]$ species. When the pL ($-\log [L]$) value equal ~ 9.5 , the $[MAL]$ nearly vanishes ($\alpha(a) \approx 2.6\%$, $\alpha(b) \approx 2.3\%$), while in case of MAL_2 precipitation starts to appear which may be due to steric hindrance offered by the tendency of azopyrimidine ligand to form polymer as well as its ability to form different types of chelate rings [41]. Thus, the coordination of the second ligand $[L]$ to MAL ternary complexes may lead to an increase in the size of the chelate ring and change in the geometry of MAL_2 complexes compared to MAL ones.

Structure of Complexes

The electronic spectra of the solid complexes in DMF solution Fig (10) show broad band in the $29000\text{--}24000\text{ cm}^{-1}$ region. The spectra of all complexes are characterized by one or more broad band in the $29000\text{--}24000\text{ cm}^{-1}$ region corresponding to an intermolecular CT transition from the antibonding level of the ligand to the vacant orbital of metal ion ($L \rightarrow M$ CT).

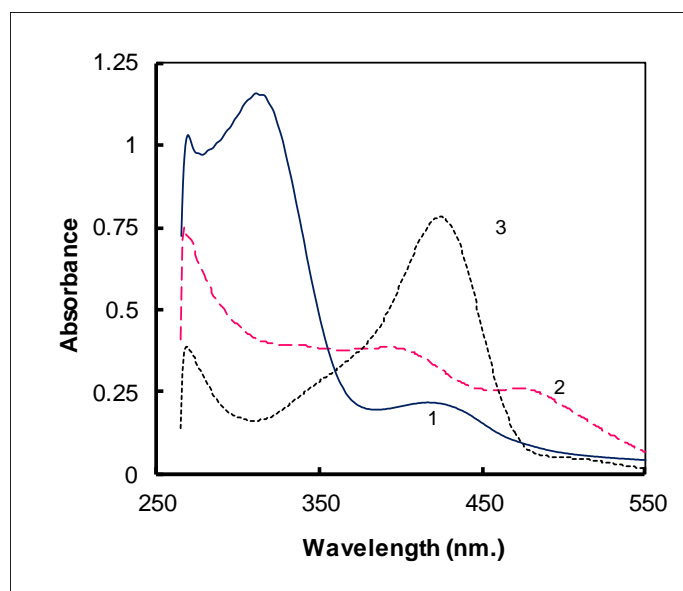


Figure 10 Electronic absorption spectra in DMF of solid complexes of L_2 with 1-Cu(II), 2-Co(II), and 3-Ni(II)

The broad shape of this band influenced by the nature of both metal ion and, substituent is in line with its assignment. Moreover, the electronic structure of the d-metal complexes can be explained on the basis of the electronic configuration of Co ($3d^7$), Ni ($3d^8$), and Cu ($3d^9$) electrons in the d-orbitals [44]. The Ni(II) has two unpaired electrons (even number) in the $3d$ level, while Co(II) and Cu(II) have one (odd number) unpaired electrons. The pairing effect of the unpaired electrons can occur for Co(II) and Ni(II), while Cu(II) electrons can't pair where no empty inner (d) orbital will be available to form $3d$, $4s^2$, sp^2 hybrid for square planar structure, and, thus, Cu(II) is expected to be either tetrahedral structure with $4s$, $4p^3$ hybridization, or distorted square pyramidal ($4s$, $4p^3$, $4d^2$) structure. On the other hand, Co(II) and Ni(II) may be formed square planar (d , s , p^2) structure due to the $d_{x^2-y^2}$ orbital will be empty. The weak shoulder observed at lower energy side is ascribed to d-d transition within the high-spin octahedral geometry. This leads to splitting the ground state ${}^4T_{1g}(F)$ of Co(II) under the influence of the octahedral field to three fold-degeneracy which may be assigned as v_1 (${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$), v_2 (${}^4T_{1g}(F) \rightarrow {}^4A_{1g}(F)$) and v_3 (${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$) [45]. The Ni(II) complexes are expected to be diamagnetic, and, thus, may exhibit square-planar geometry. Diamagnetism is resulted from the pairing of the d^8 electrons in four lower lying d-orbitals. These lower orbitals are so close together in energy that individual transition from each orbital to upper (d) level can be distinguished, and,

hence, they may appear as a single band. Thus, the observed shoulders may be due to spin-orbital coupling which mixes the very close ${}^3T_{1g}(F)$ and 1E_g starts, expected for square planar or distorted octahedral geometry according to ${}^3A_{1g}(F) \rightarrow {}^3T_{1g}(F)$.

IR Spectra

The vibration spectra of the prepared free ligands exhibit a very broad band at around 3450 cm^{-1} due to the ν_{OH} and two weak bands in the region $3290\text{--}3035\text{ cm}^{-1}$ assigned to the ν_{NH_2} stretching vibration of C(2), C(4)-NH₂ of the pyrimidine ring. The broad shape of these bands can be attributed to the possible formation of intramolecular H-bond between the pyrimidine OH or NH₂ groups and the azo group [46]. On complexation with Cu(II), Ni(II) and Co(II) ions, the above mentioned bands are affected to different degrees. The ν_{OH} band shows change in the shape and position which appeared as a medium or strong feature. One of the vibration modes of ν_{NH_2} is absent, while the other one is blue shifted in Cu(II) complexed or still remained in the same position in case of Ni(II) and Co(II) complexes. These data indicate that both nitrogen (amino) and oxygen (OH) atoms are active sites for complexation. Previous studies on similar compounds have revealed that the coordination through the exocyclic oxygen is preferable than the NH₂ group [47,48]. On the other hand, the strong and broad bands observed in complexes around 3300 cm^{-1} weak with shoulder at ~ 3750 which have significantly different characteristics from the H-bonded ν_{N-OH} vibrations. These bands are attributed to the presence of water molecules in the complexes prepared. Since, it was known that the free water is absorbed at 3520 cm^{-1} [49]. The weak and medium bands at 3150 and 2840 cm^{-1} region can be assigned to the ν_{NH} stretching modes. The presence of these band suggests that the pyrimidine hetero-N atom at N(1) and N(3) may be protonated or due to the H-bonded NH of amino groups. This is based on the possible migration of proton from OH and NH₂ groups to the adjacent hetero nitrogen atom. This behaviour suggests that the studied compound can exist in keto-enol tautomeric equilibrium [50]. The two weak and broad bands located at around 1610 and 1550 cm^{-1} can be attributed to the heterocyclic ring $\nu_{C=N}$ stretching vibrations. The band at around 1270 cm^{-1} is assigned to ν_{C-N} (of NH₂) in agreement with earlier publications [51,52]. On complexation the $\nu_{C=N}$ and ν_{C-N} stretching vibrations show lower shift which supports the involvement of NH₂ in chelate ring. The observed blue shift in these band may be due to the decrease of the bond order of carbon to the nitrogen link following the coordination of the imine nitrogen atom to metal ions. The studied free ligands show two strong IR bands in the region $1500\text{--}1455\text{ cm}^{-1}$ and around 1385 cm^{-1} are due to the $\nu_{N=N}$ mode [51]. In Cu(II) and Ni(II) complexes, these two bands are absent or shifted from their positions to lower wave numbers by $\sim 50\text{ cm}^{-1}$ relative to the uncoordinated ligands and appeared as weak band in Co(II) complexes, so the nitrogen atom of N=N group is involved in structural configuration. The spectra of the reagents with transition elements under study can act in a N, N or N, O bidentate manner through the N-(or OH) atom of NH₂ or OH and N-atom of N=N group in the region $1500\text{--}1455\text{ cm}^{-1}$ and around 1385 cm^{-1} . In Co(II) (M:L) complexes and in 2M:L these ligands can act as tridentate through the two nitrogen of NH₂ 1622 cm^{-1} and the hetero nitrogen of the pyrimidine ring.

¹H- NMR Spectra

The ¹H NMR spectra of the free ligands signals are appearing at 10.03-11.08 ppm which is attributed to the NH proton associated to the pyrimidine ring N(1), N(3) and hydrazone NH proton [53-55]. The signal at 8.48-9.01 ppm range is in position observed for the hydrogen bonded OH proton of pyrimidine C(6) ring. The presence of the above two signals suggested that the ligands under study do not exclusively exist in hydroxy azo structure, but they contain some amount of azoquinone hydrazone tautomers. The two forms are resulted from the mobility of OH or NH₂ protons which lead to form extensively hydrogen bonded. These ligands can form an intramolecular H-bond between the C(4) NH₂ hydrogen or the pyrimidine C(6) OH hydrogen and N=N group, as well as, an intermolecular H-bond involves NH₂ or OH hydrogen and the adjacent heterocyclic N(1) or N(3) atom. It is found that the migration of the labile proton to the nitrogen atom depends on the relative basicities of the OH, NH₂, N=N groups and N(1), N(3) nitrogen. The NH₂ protons of the free ligands appear as split signals between 4.42 [C(2)-NH₂] and 5.89 [C(6)-NH₂] ppm. The non equivalence of the hydrogen atoms of the NH₂ groups could be attributed to the NH---N hydrogen

banding formation. Owing to this bond, the resonances of the two NH₂ groups of the pyrimidine ring occur in different chemical shifts. Moreover, the higher field NH₂ group is assigned to the C(6) NH₂ protons because its nearby the azo group has a deshielding effect. This indicates that the ligands under study contain some amount of azoquinone hydro tautomers. These signals are absent in complexes indicated its involvement in coordination. The proton of arylazo system appears as broad multi signal at 6.50 to 7.77 ppm. The multiplet nature of this signals can be attributed to the shielding effect of N=N group which shields the para-hydrogen more strongly than the ortho-hydrogen as a result of a mesomeric effect, while the meta-hydrogen is the least shielded. Therefore, the aromatic ring signals appear as multiplet which the para proton resonates upfield relative to that of meta ones. The combination of the IR and ¹HNMR results reveals that ligands can exist in the keto-enol form.

Conclusion

The overall formation constants of 1:1:1 ternary complexes of Cu(II), Co(II), Ni(II) with Glycine (Gly), DL- Alanine (Ala) and Glutamic Acids (Glu) as primary and 5-(arylozo)2,6-diamino-4-pyrimidinol as secondary ligands as well as those of the binary systems have been investigated potentiometrically in 40% (v/v) EtOH-H₂O at 25 °C and I=0.15 M NaClO₄. The Cu(II), Co(II) and Ni(II) complexes have been synthesized and the coordination sites of the ligands were characterized by IR and ¹HNMR. The stability order of binary system decreases in the order Gly > Ala > Glu. The concentration distribution of various species formed in solution was evaluated spectroscopy.

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Publication History

Received 03rd July 2014
Revised 20th July 2014
Accepted 14th Aug 2014
Online 30th Aug 2014