pH-metric and Spectrophotometric Studies on the Binary and Ternary Complexes of Copper(II) with 2,3-Pyrazinedicarboxylic Acid and Some Aliphatic and Aromatic Acids

by M.K.M. Rabia[1][*], H.A. Al-Gwidi[2] and K.A.A. Al-Ibrahem[2]

[1]*Chemistry Department, Faculty of Science, South Valley University, Sohag, Egypt*
[2]*Girl's College of Education, Scientific Departments (Chemistry), Riyadh, KS.A*

Formation and stability of binary and ternary complexes of copper(II) with 2,3-pyrazine-dicarboxylic acid as a primary ligand and some biologically important aliphatic, aromatic and heteroaromatic carboxylic acids (succinic, malic, anthranilic, phthalic, salicylic, thiosalicylic and 2-hydroxynicotinic acids) as secondary ligands were determined by potentiometric and spectrophotometric techniques. The determination were performed in a 20% (v/v) ethanol-aqueous medium. Δlog K and log X values indicate the favoured formation of ternary complexes, compared to the binary ones. The order of stability of the complexes under investigation in terms of the nature of secondary ligands is examined and discussed.

Key words: pH-metric, 2,3-pyrazinedicarboxylic acid, ternary complexes and spectrophotometric

Although solid complexes of 2,3-pyrazinedicarboxylic acid have been the subject of intensive research [1–9], the complex equilibria of this ligand with metal ions have received relatively little attention [10,11]. As a continuation of our earlier work [12] on the stability constant of binary and ternary complexes involving Zn(II) and Cd(II) metal ions with 2,3-pyrazinedicarboxylic acid, the present investigation traces the formation and characterization of binary and ternary complexes of copper(II) with 2,3-pyrazinedicarboxylic acid as a primary ligand and aliphatic, aromatic and heteroaromatic carboxylic acids as secondary ligands. The secondary ligands are malic (mal), succinic (suc), anthranilic (anth), phthalic (phth), salicylic (sa), thiosalicylic (tsa) and 2-hydroxynicotinic (hyna) acids. The stability of the formed complexes has been determined potentiometrically and spectrophotometrically.

[*]Corresponding author, E-mail: mostafarabia@hotmail.com

EXPERIMENTAL

2,3-Pyrazinedicarboxylic acid was obtained from Fluka. Stock solutions were prepared by dissolving precisely weighed amounts of the acid in bidistilled water. Copper nitrate was provided by BDH. A stock solution of copper(II) nitrate was prepared and standardized complexometrically by EDTA. Ethanol was obtained from BDH (spectro grade product). Carbonate-free potassium hydroxide (titrant, prepared in 0.1 mol dm^{-3} KNO_3 solution) was standardized potentiometrically with KH-phthalate solution (BDH-AR). Aliphatic, aromatic and heteroaromatic carboxylic acids, nitric acid and KOH were from BDH. Other chemicals were of AR grade. All the secondary ligand solutions (5.0×10^{-2} mol dm^{-3}) were prepared in 20% (v/v) ethanol-aqueous solution. Buffer solutions were prepared as described previously [13].

pH-metric measurements were performed on a Beckman $\Phi 70$ pH-meter equipped with a combined glass electrode. The correction of pH readings in ethanol-aqueous medium were made as described elsewhere [14]. The absorption spectra of solutions were recorded on a UV- VIS 160A-UV spectrophotometer in the range 200–500 nm using 1-cm matched silica cells. All the potentiometric and spectrophotometric measurements were performed in 20% (v/v) ethanol-aqueous medium at 298 K. The ionic strength of all solutions measured was adjusted to $\mu = 0.1$ mol dm^{-3} (KNO_3).

RESULTS AND DISCUSSION

Potentiometric studies: The dissociation constants of cationic 2,3-pyrazinedicarboxylic acid, $PyzdcH_3^+$, could not be calculated potentiometrically, because of the highly acidic nature of the associated proton (pKa = –3) [11].

Figure 1 displays a representative set of experimental titration curves obtained in (20% v/v) ethanol-aqueous medium, according to the above described sequence for the different $Cu^{2+} - pyzdcH_2 -$ aliphatic or aromatic and heteroaromatic acid systems. The potentiometric titration curve for the subject pyrazine ligand, $pyzdcH_2$ (curve b, Fig. 1), shows two inflection points at a = 1 and 2 (where a = C_{OH}/C_{PyzdcH_2}). The acid dissociation constants of this ligand (pK_{a1} and pK_{a2}) are determined under the identical conditions from the titration curves (a) and (b) making use of the Irving and Rossotti formulation [15,16]. The obtained data are given in Table 1. The two steps corresponding to the proton-dissociation involved in the titration of $pyzdcH_2$ can be represented as follows:

$$pyzdcH_2 \rightleftharpoons pyzdcH^- + H^+, K_1 \tag{1}$$

$$pyzdcH^- \rightleftharpoons pyzdc^{2-} + H^+, K_2 \tag{2}$$
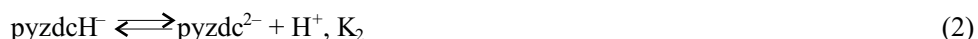
The titration curve (c) (*cf*. Fig. 1) for a mixture of Cu(II) and the pyrazine ligand exhibits two inflection points at m = 1 and m = 2 (where m = C_{OH}/C_M). This curve clearly indicates, that binary complexes of 1:1 and 1:2 stoichiometric ratios, $[Cu(pyzdcH)]^+$ and $[Cu(pyzdcH)_2]$, are formed at pH ranges of 3.5–5.5 and 6.5–10.0, respectively. This is achieved from the apparent divergence of the 1:1 and 1:2 binary Cu(II)-$pyzdcH_2$ titration curve from that of the corresponding free ligand (curves (c) and (b), respectively).
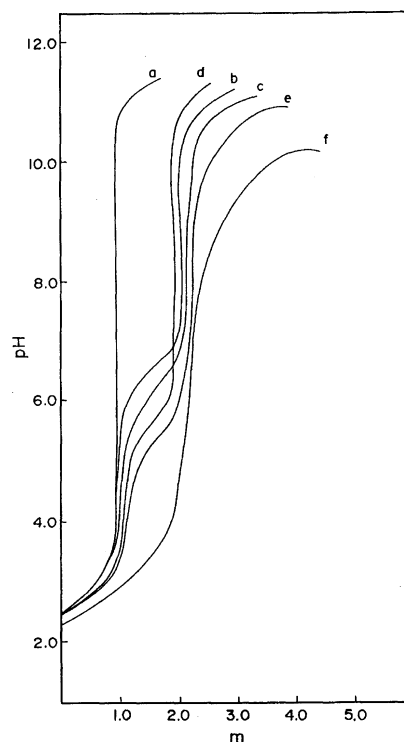
Figure 1. Potentiometric titration curves of binary and ternary complex system for [Cu(II)–pyzdcH$_2$– anthranilic acid] in 20% (v/v) ethanol at 298 K, $\mu = 0.1$ mol dm^{-3} [a, HNO$_3$; b, a + pyzdcH$_2$; c, a + b + Cu(II); d, a + anth; e, d + Cu(II); f, a + pyzdcH$_2$ + anth + Cu(II)].
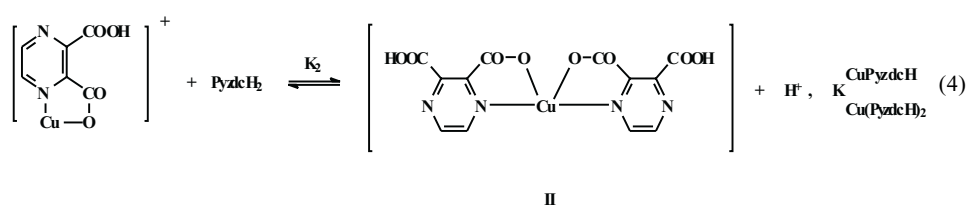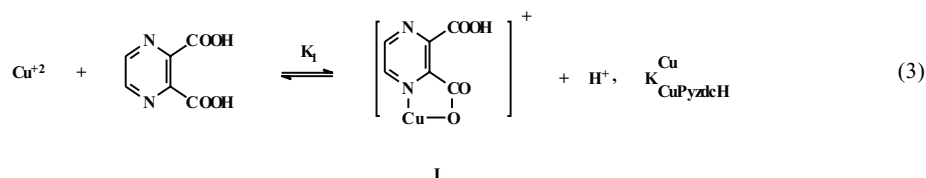
Table 1. pK$_a$ values[a] of ligands and stability constants of their 1:1 and 1:2 binary complexes[b,c] of Cu(II) in 20% (v/v) ethanol at 298 ± 0.1 K, $\mu = 0.1$ mol dm^{-3} (KNO$_3$).

Ligand (L)	pK$_{a1}$	pK$_{a2}$	logK$_{CuL}^{Cu}$	logK$_{CuL_2}^{CuL}$	ΔlogK	logβ$_{CuL_2}^{Cu}$
pyzdcH$_2$	2.77	4.06	4.92	4.54	−0.38	9.46
mal	3.45	5.10	4.80	4.08	−0.72	8.88
suc	4.55	6.00	4.84 (4.75[20])	4.16 (4.25[20])	−0.68	9.00
anth	–	6.40	5.46 (5.75[20])	4.80 (4.90[20])	−0.66	10.3
phth	2.89	6.26	6.60	5.86	−0.79	12.5
sa	5.74	13.6[d]	10.68 (10.62[20])	10.50 (10.10[20])	−0.53	20.8
tsa	5.46	8.95	6.84 (7.60[20])	6.08 (6.90[21])	−0.76	12.9
hyna	6.50	10.60	7.43	6.83	−0.60	14.3

[a]All constants are accurate to ± 0.03; [b]all constants are accurate to ± 0.06; [c]accuracy is $\pm 1\%$ and [d]Ref. [20]. Literature values are given in parentheses.

This behaviour strongly suggests that the subject pyrazine ligand is characterized by a high tendency to form metal complexes. The stepwise reaction of Cu(II) with pyzdcH$_2$ may proceed in either of the two following ways:

(a)

$$Cu^{+2} \;+\; \text{(pyzdcH}_2\text{)} \quad \overset{K_1}{\rightleftharpoons} \quad [\text{I}]^{+} \;+\; H^{+}, \quad K_{CuPyzdcH}^{Cu} \qquad (3)$$

I

$$[\text{I}]^{+} \;+\; PyzdcH_2 \quad \overset{K_2}{\rightleftharpoons} \quad [\text{II}] \;+\; H^{+}, \quad K_{Cu(PyzdcH)_2}^{CuPyzdcH} \qquad (4)$$

II

(b)

$$Cu^{+2} \;+\; 2\,\text{(pyzdcH}_2\text{)} \quad \overset{K}{\rightleftharpoons} \quad [\ ]^{2-} \;+\; 4\,H^{+} \qquad (5)$$
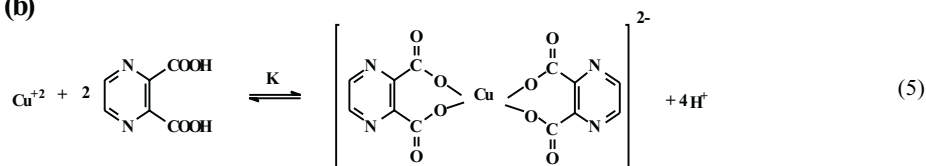
If reaction takes place according to pathway (a), the first inflection point (m = 1) corresponds to the formation of species (I) and the second inflection point (m = 2) corresponds to the complete neutralization of species (II) [Cu(pyzdcH)$_2$]. However, if the pathway (b) is taking place, then one would expect that the titration curve exhibits only one inflection point at $C_{OH}/C_M = 4.0$. On the other hand, the titration curve of the Cu(II)-pyzdcH$_2$ mixture has inflection points, which resemble to a great extent the titration of a dicarboxylic acids alone [17,18]. This indicates that the reaction of Cu(II) with pyzdcH$_2$ follows the reaction pathway (a).

In binary systems involving Cu(II) with pyzdcH$_2$, the formation constants for (3) and (4) were determined from the titration curves (b) and (c) making use of the Irving and Rossotti formulation [15,16]. The obtained values are included in Table 1. The $\Delta \log K = (\log K_{CuL_2}^{CuL} - \log K_{CuL}^{Cu})$ value for Cu(II) – pyzdcH$_2$ complex is negative (*cf.* Table 1). This is expected from the statistical consideration, that the stability constants of 1:2 complexes are lower than those of the corresponding 1:1 ones.

The pKa values of malic, succinic, anthranilic, phthalic, salicylic, thiosalicylic and 2-hydroxynicotinic acids and the log K values of their binary Cu(II) complexes were determined by the method of Irving and Rossotti [15,16]. This method was applied to the pH-titration curves of free ligands (curve d) and of binary complex solu-

tions (curve e) (*cf*. Table 1). The various binary complexes formed are in the 1:1 and 1:2 stoichiometric ratios (M:L). The agreement between our and the literature values is fairly good (*cf*. Table 1) [19,20].

Ternary systems: Potentiometric titration curves (Fig. 1, curve f) for ternary systems containing Cu(II), $pyzdcH_2$ and anth, mal or sa in a 1:1:1 molar ratio exhibit a single steep inflection at m = 2. In ternary systems involving suc, phth, tsa or hyna as the secondary ligand, an inflection is obtained at m = 3. The analysis of the titration curves for the ternary systems indicates that ternary complexes are formed in all the systems investigated. Stability constants for the formation of ternary complexes, according to the equilibrium (6), are listed in Table 2.

$$Cu(pyzdcH) + L \rightleftharpoons Cu(pyzdcH)L \tag{6}$$

Table 2. Stability constants for Cu(II)–$pyzdcH_2$-L systems in 20% ethanol at 298 ± 0.1 K, $\mu = 0.1$ mol dm^{-3} (KNO$_3$).

Ligand (L)	$\log K_{Cu(pyzdcH)L}^{CuL}$	$\log \beta_{Cu(pyzdcH)L}^{Cu}$	$\Delta \log K$	Log X
mal	5.08	10.00	0.28	1.60
suc	5.16	10.1	0.32	1.70
anth	5.81	10.7	0.35	1.74
phth	7.03	11.9	0.43	1.98
sa	11.37	16.3	0.69	2.29
tsa	7.29	12.2	0.45	2.04
hyna	8.02	12.9	0.59	2.16

The relative stabilities of the ternary complexes, as compared to the corresponding binary ones, can be quantitatively expressed in two ways [21,22]. In one approach the stability of the ternary complex is compared with those of the bis binary complexes in terms of the disproportionation constant (X) for the equilibrium (7).

$$Cu(pyzdcH)_2 + CuL_2 \rightleftharpoons 2Cu(pyzdcH)(L) \tag{7}$$
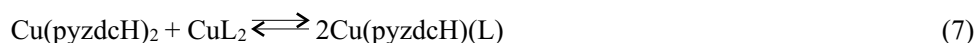
$$X = [Cu(pyzdcH)(L)]^2/[Cu(pyzdcH)_2][CuL_2] \tag{8}$$

$$\log X = 2\log\beta_{Cu(pyzdcH)L}^{Cu} - (\log\beta_{Cu(pyzdcH)_2}^{Cu} + \log\beta_{CuL_2}^{Cu}) \tag{9}$$

The statistical value for log X (approximately equals 0.6) [22,23] is the same for all geometries for the coordination sphere of a metal ion. The other approach is in terms of Δlog K, which represents the difference in stability for the addition of secondary ligand to the 1:1 Cu(pyzdcH) complex and to the aquated metal ion (10)

$$\Delta logK = logK_{Cu(pyzdcH)L}^{Cu(pyzdcH)} - logK_{Cu(pyzdcH)}^{Cu} = logK_{CuL(pyzdcH)}^{CuL} - logK_{CuL}^{Cu} \tag{10}$$

It has been shown that for a variety of reasons [21], a comparison under the experimental conditions of this study in terms of $\Delta log K$ will be more convenient. The differences in the stabilities of the binary and ternary complexes in terms of $\Delta log K$ are given in Table 2. For all the systems, the $\Delta log K$ values are positive showing that the equilibrium

$$Cu(pyzdcH) + CuL \rightleftharpoons Cu(pyzdcH)L + Cu \tag{11}$$
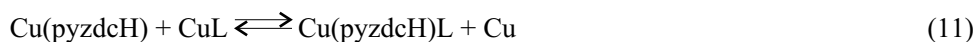
is favored towards the right hand side [24].

The experimental data show that the formation of the ternary complex of Cu^{2+} with pyzdcH$_2$ and secondary ligands shifts the buffer region of the ligand to lower pH values, which indicates that the ternary complex is more stable than the binary complex. Further, the deprotonation of pyzdcH$_2$ in the ternary system occurs at a lower pH than that of the corresponding binary complex. This means that the ternary Cu–pyzdcH–L complex is more stable than the Cu–pyzdcH binary complex and hence a positive $\Delta log K$ value was obtained.
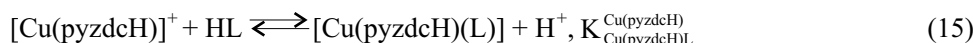
The overall stability constant $\beta_{Cu(pyzdcH)L}^{Cu}$, which must be determined experimentally, is related to $K_{Cu(pyzdcH)L}^{Cu(pyzdcH)}$ and $K_{CuL(pyzdcH)}^{CuL}$ by (12) and (13) respectively.

$$logK_{Cu(pyzdcH)L}^{Cu(pyzdcH)} = log\beta_{Cu(pyzdcH)L}^{Cu} - logK_{Cu(pyzdcH)}^{Cu} \tag{12}$$

$$logK_{CuL(pyzdcH)}^{CuL} = log\beta_{CuL(pyzdcH)}^{Cu} - logK_{CuL}^{Cu} \tag{13}$$

On the bases of the above results, the possible equilibria for the $Cu - pyzdcH_2 - L$ ternary complexes can be represented as follows:
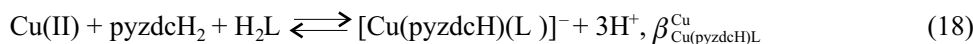
For Cu(II) – pyzdcH$_2$ – anth ternary systems:

$$Cu(II) + pyzdcH_2 + HL \rightleftharpoons [Cu(pyzdcH)(L)] + 2H^+, \beta_{Cu(pyzdcH)L}^{Cu} \tag{14}$$

$$[Cu(pyzdcH)]^+ + HL \rightleftharpoons [Cu(pyzdcH)(L)] + H^+, K_{Cu(pyzdcH)L}^{Cu(pyzdcH)} \tag{15}$$

For Cu(II) – pyzdcH$_2$ – mal or sa ternary systems:

$$Cu(II) + pyzdcH_2 + HL^- \rightleftharpoons [Cu(pyzdcH)(L)]^- + 2H^+, \beta_{Cu(pyzdcH)L}^{Cu} \tag{16}$$

$$[Cu(pyzdcH)]^+ + HL^- \rightleftharpoons [Cu(pyzdcH)(L)]^- + H^+, K_{Cu(pyzdcH)L}^{Cu(pyzdcH)} \tag{17}$$
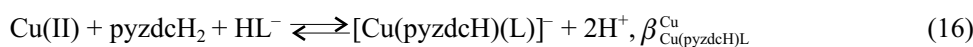
For Cu(II) – pyzdcH$_2$ – tsa, phth, suc or hyna ternary systems:

$$Cu(II) + pyzdcH_2 + H_2L \rightleftharpoons [Cu(pyzdcH)(L)]^- + 3H^+, \beta_{Cu(pyzdcH)L}^{Cu} \tag{18}$$

$$[Cu(pyzdcH)]^+ + H_2L \rightleftharpoons [Cu(pyzdcH)(L)]^- + 2H^+, K_{Cu(pyzdcH)L}^{Cu(pyzdcH)} \tag{19}$$

The acidity constants of the ligands and the stability constants of the binary Cu(II) complexes used for calculation of the stability constants of the ternary complexes are listed in Table 1. The results obtained for the formation of ternary complexes between the Cu(II)–pyzdcH$_2$ (1:1) complex and suc, mal, anth, phth, sa, tsa and hyna are shown in Table 2. The constant calculated from the experimental data was log $\beta_{\text{CuL(pyzdcH)L}}^{\text{Cu}}$, which is derived from the overall equilibrium.

$$Cu + pyzdcH_2 + L \rightleftharpoons Cu(pyzdcH)(L) \tag{20}$$

Using the results in Tables 1 and 2, the values for Δlog K (Eq. 10) and logX (Eq. 9) were calculated and are summarized for all mixed-ligand systems in Table 2. A comparison of the stability constants of the ternary complexes indicates, that the order of stability in terms of the secondary ligand is: mal < suc < anth < phth < tsa < hyna < sa. The relative stabilities of the ternary complexes of salicylic acid and thiosalicylic acid follow their relative basicities. Moreover, the order of stabilities of mixed-ligand complexes of aliphatic acids is in accordance with the basicities (pK$_{a1}$ + pK$_{a2}$) of the ligands. It is well known, that the increase in basicity of a ligand increases the stability of its metal complexes. The higher values of Δlog K with aromatic acids than aliphatic acids may be attributed to the presence of an aromatic ring [25], which alters the bonding properties of these carboxylic acids. It is also observed that, Δlog K values is more positive for tsa ternary complex (0, S donor ligand) than for anth (0, N donor) ternary complex. The observed trend may be explained as follows: since sulphur is one of the most important donor atoms *in vivo* as well as *in vitro*, it is able to form both σ and π bands [26]. The stability increase of the ternary complex has been attributed to d$_\pi$-d$_\pi$ interactions of metal d-orbitals to vacant d-orbitals available on sulphur atom in tsa. The M − S$_\pi$ interactions have also been considered to affect the formation constant of the ternary complex [27]. The lower magnitude of positive ΔlogK value with anth (0, N donor ligand) may be due to the fact that anth is coordinated to the metal ion in such a way that the benzene ring is coplanar with the rest of the complex molecule, since the amino and carboxylic groups are in the orthopositions [28].

Spectrophotometric studies: The absorption spectra of 2.5×10^{-4} mol dm^{-3} solution of 2,3-pyrazinedicarboxylic acid (pyzdcH$_2$) were recorded as the dependence A = f(λ) for various pH and in the presence of 20% (v/v) ethanol at 298 K of 0.1 mol dm^{-3} (KNO₃). The spectra of the subject pyrazine ligand display an absorption band at 278–282 nm within the pH range 2.5–11.0. The absorption spectra of the reaction of Cu^{2+} with pyzdcH$_2$ in equimolar concentrations (1:1) in the pH range of study against reagent blank as reference exhibit an absorption band at λ_{max} = 292 nm. Moreover, the spectra of Cu^{2+} with the different secondary ligands (sa, tsa or hyna) in equimolar concentrations (1:1) display absorption bands at 278, 297 and 305 nm, respectively with the pH range: pH = 5–7 (sa), 7–8 (tsa), and 6.5–7.5 (hyna). However, the spectrum of the ternary systems containing equimolar concentrations of Cu^{2+}, pyzdcH$_2$ and sa, tsa or hyna as secondary ligands against a blank solution containing the same

concentration of the two ligands exhibits new bands at 296, 302 and 319 nm respectively.

Stoichiometry of the complex: The stoichiometry of the ternary Cu^{2+} – pyzdcH$_2$ – sa, tsa or hyna complexes was traced by Job's method of continuous variations [29,30]. The molar fraction of two of the components was varied continuously, keeping their combined concentration constant and the third component in a large constant excess for all solutions in the series. Under these conditions, the ternary system was modified to a quasi-binary system. The results, shown graphically in Fig. 2, indicate that the overall Cu(II) – pyzdcH$_2$ – sa composition is 1: 1: 1 at the pH used. The composition of the ternary systems with tsa and hyna was also found to have the same ratio. The stoichiometry of the ternary system was also determined by applying the molar ratio method [31] (*cf.* Fig. 3).
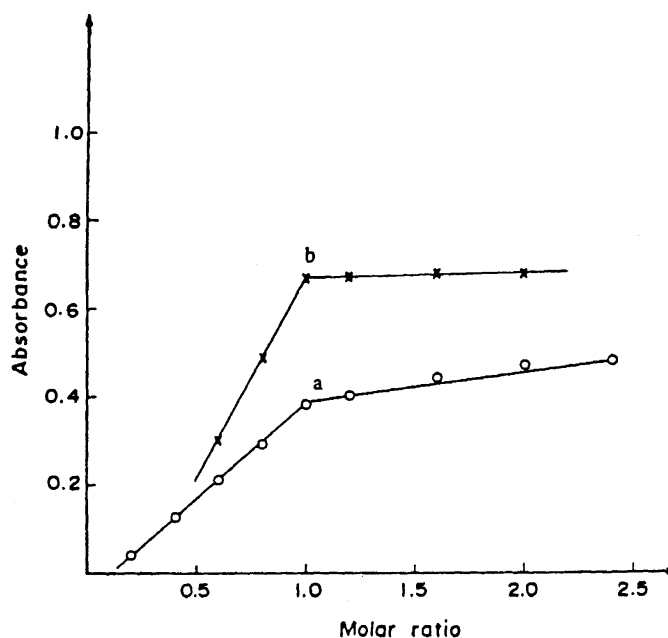

Figure 2. Molar ratio plots: a)Variation of pyzdcH$_2$ in the range of 2.5×10^{-5}–3.75×10^{-4} mol dm^{-3} at constant $[Cu^{2+}] = 1.25 \times 10^{-4}$ mol dm^{-3} in the presence of 5.0×10^{-4} mol dm^{-3} sa. b) Variation of sa in the range of 2.5×10^{-5}–3.75×10^{-4} mol dm^{-3} at constant $[Cu^{2+}] = 1.25 \times 10^{-4}$ mol dm^{-3} in the presence of 5.0×10^{-4} mol dm^{-3} pyzdcH$_2$.

Determination of the stability constant of ternary complex: The formation of the ternary complex was investigated at different pH using equimolar concentration of components. The absorbance *versus* pH graphs at 296 nm (*cf.* Fig. 4) indicate the existence of two basic equilibria within the pH range of study. These graphs were analysed graphically, using the relations derived elsewhere [32,33]. The analysis of the two rising parts of these graphs were performed assuming the following scheme:
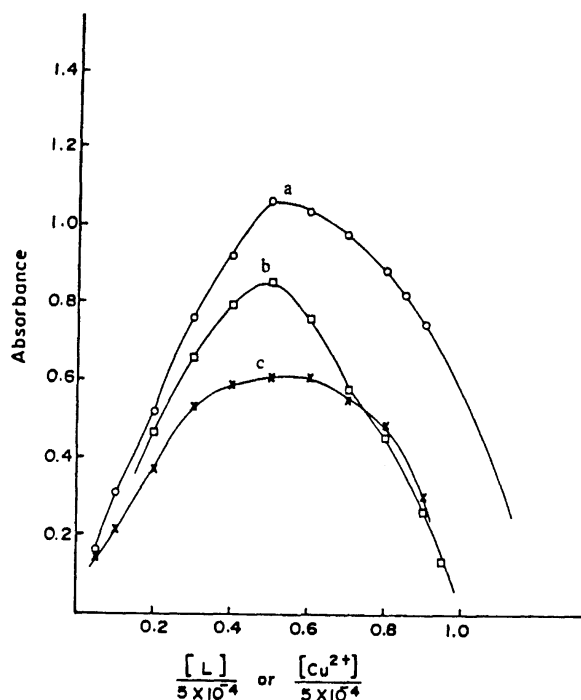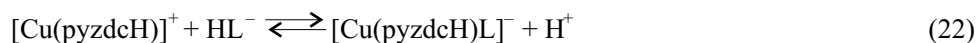
Figure 3. Job's plots: a) Cu^{2+}– sa (in the presence of excess pyzdcH$_2$). b) sa – pyzdcH$_2$ (in the presence of excess Cu^{2+}). c) Cu^{2+} – pyzdcH$_2$ (in the presence of excess sa).

$$Cu^{2+} + pyzdcH_2 \rightleftharpoons [Cu(pyzdcH)]^+ + H^+ \tag{21}$$

$$[Cu(pyzdcH)]^+ + HL^- \rightleftharpoons [Cu(pyzdcH)L]^- + H^+ \tag{22}$$

The molar absorptivity ε_2 of the copper ternary complex was estimated by

$$C_M/\Delta A = 1/\varepsilon_2 + (\Delta A - \varepsilon_1 C_M)[H]^q Z/\Delta A K_1 \varepsilon_2 C_L \tag{23}$$

Where ε_1 and ε_2 are the molar absorptivities of the $[Cu(pyzdcH)]^+$ and $[Cu(pyzdcH)L]^-$ complexes, respectively and $Z = 1 + K_{a1}/[H]$. This transformation was linear, assuming the release of one proton ($q = 1$) during the formation of the ternary complex according to (22). The number of liberated protons (q) as well as the equilibrium constant of reaction (22) were obtained using (24).

$$Log[(\Delta A - \varepsilon_1 C_M)Z/(\varepsilon_2 C_M - \Delta A)] = qpH + logC_L + logK_2 \tag{24}$$

Table 3 contains the results obtained for the molar absorptivities, equilibrium constants and stability constants of the binary and ternary complexes under investigation. By comparison of both potentiometric and spectrophotometric results it is found that: 1) The stoichiometric ratio of the subject ternary complexes determined by the
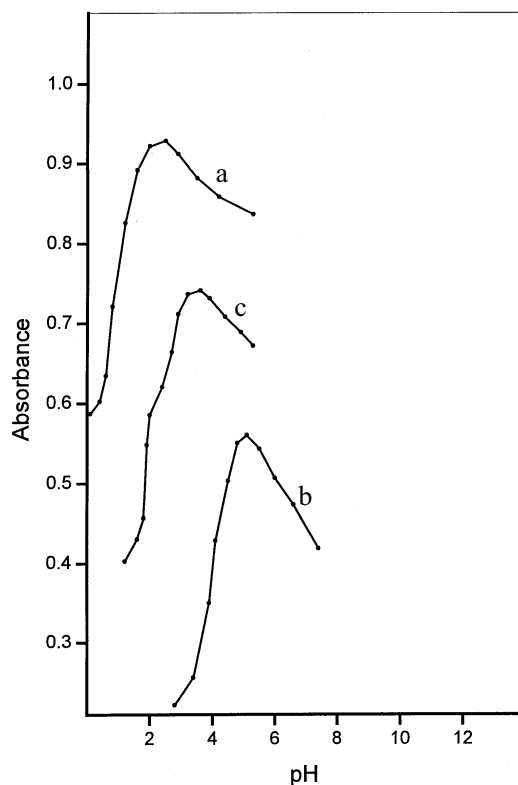
Figure 4. Absorbance *versus* pH graphs for binary and ternary systems, 20% (v/v) ethanol: a) Cu^{2+} – pyzdcH$_2$ binary system, $C_L = C_M = 2.5 \times 10^{-4}$ mol dm^{-3}, $\lambda = 292$ nm. b) Cu^{2+} – sa binary system, $C_L = C_M = 2.5 \times 10^{-4}$ mol dm^{-3}, $\lambda = 278$ nm. c) Cu^{2+} – pyzdcH$_2$–sa ternary system, $C_L = C_M = 2.5 \times 10^{-4}$ mol dm^{-3}, $\lambda = 296$ nm.

two methods is the same (1:1:1 ratios). 2) There is a significant difference in the logβ value in the two methods. This difference is in agreement with findings of other workers [19] for the system Cu–3-hydroxypicolinamide–tsa as shown from the following data:

	Potentiometric	Spectrophotometric	
	16.4	20.3	ref. [19]
logβ			
	12.21	16.07	our data

These data show, that the logβ values exhibit approximately the same differences in both techniques.

Table 3. Mean values of equilibrium constant (log K), stability constant (logβ) and molar absorptivity (ε) of the ternary copper(II) complex with pyzdcH$_2$ and sa, tsa or hyna in 20% (v/v) ethanol at 298 ± 0.1 K, $\mu = 0.1$ mol dm^{-3} (KNO$_3$).

Equilibrium	Con-stant	log constant			Molar absorptivity L mol^{-1} cm^{-1} $\times 10^{-4}$		
		sa	tsa	hyna	sa	tsa	hyna
[Cu(pyzdcH)(L)][H]/[Cu(pyzdcH)][HL]	K	–2.15	–2.30	–2.45			
					1.45	0.85	1.10
[Cu(pyzdcH)(L)]/[Cu][pyzdcH][L]	β*	20.7	16.1	17.7			

*logβ = log K + log$\beta_{Cu(pyzdcH)}$ + pK$_{a(pyzdcH)}$ + pK$_{a2}$ (secondary ligand).

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