

## ***Fac-mer* equilibria of coordinated iminodiacetate ( $\text{ida}^{2-}$ ) in ternary $\text{Cu}^{\text{II}}(\text{ida})(\text{H}_{-1}\text{B})^-$ complex formation (B = imidazole, benzimidazole) in aqueous solution**

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**Abstract.** pH potentiometric and spectrophotometric investigations on the complex formation equilibria of  $\text{Cu}^{\text{II}}$  with iminodiacetate ( $\text{ida}^{2-}$ ) and heterocyclic N-bases, viz. imidazole and benzimidazole (B), in aqueous solution in binary and ternary systems using different molar ratios of the reactants indicated the formation of complexes of the types,  $\text{Cu}(\text{ida})$ ,  $\text{Cu}(\text{ida})(\text{OH})^-$ ,  $(\text{ida})\text{Cu}(\text{OH})\text{Cu}(\text{ida})^-$ ,  $\text{Cu}(\text{B})^{2+}$ ,  $\text{Cu}(\text{H}_{-1}\text{B})^+$ ,  $\text{Cu}(\text{ida})(\text{H}_{-1}\text{B})^-$ ,  $(\text{ida})\text{Cu}(\text{B})\text{Cu}(\text{ida})^-$  and  $(\text{ida})\text{Cu}(\text{H}_{-1}\text{B})\text{Cu}(\text{ida})^-$ . Formation constants of the complexes at  $25 \pm 1^\circ$  at a fixed ionic strength,  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ) in aqueous solution were evaluated and the complex formation equilibria were elucidated with the aid of speciation curves. Departure of the experimental values of the reproportionation constants ( $\Delta \log K_{\text{Cu}}$ ) of ternary  $\text{Cu}(\text{ida})(\text{H}_{-1}\text{B})^-$  complexes from the statistically expected values, despite their formation in appreciable amounts at equilibrium, were assigned to *fac(f)-mer(m)* equilibria of the  $\text{ida}^{2-}$  ligand coordinated to  $\text{Cu}^{\text{II}}$ , as the N-heterocyclic donors,  $(\text{H}_{-1}\text{B})^-$ , coordinate *trans-* to the N-( $\text{ida}^{2-}$ ) atom in the binary  $\text{Cu}(\text{ida})_f$  complex to form the ternary  $\text{Cu}(\text{ida})_m(\text{H}_{-1}\text{B})^-$  complexes.

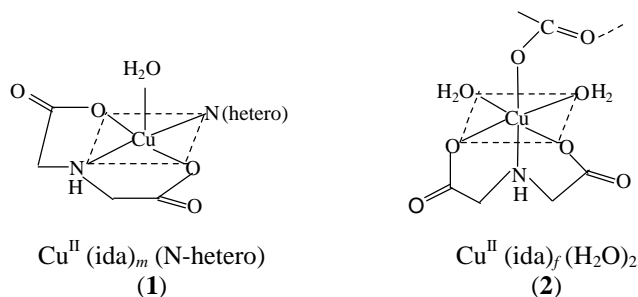
**Keywords.** *Fac-mer* equilibria;  $\text{Cu}^{\text{II}}$ -iminodiacetate-imidazole/benzimidazole ternary complexes; stability constants.

### **1. Introduction**

Mixed ligand complexes of transition metal ions with amino acids, peptides or their derivatives or analogues, and heterocyclic N-bases can serve as model compounds of bioinorganic interests, mainly because of the crucial coordinating role of the imidazole ring of histidine residue of the polypeptide chains of iron and copper proteins and enzymes,<sup>1-6</sup> and that of 5,6 dimethyl benzimidazole to cobalt in vitamin B<sub>12</sub> coenzymes.<sup>7</sup> Copper (II)-aminoacidate (or peptide or peptide like) imidazole, or benzimidazole, or related ternary complexes have been the focus of increasing interest in this context. Recently single crystal X-ray studies on 1:1:1 and 1:1:2 mixed ligand copper (II)-iminodiacetate ( $\text{ida}^{2-}$ ) or  $\text{ida}^{2-}$  like – N-heterocyclic base complexes revealed interesting structural correlations.<sup>8-11</sup> The most remarkable feature in this context is the preference of the first incoming N-heterocyclic donor for the position *trans-* to the Cu–N( $\text{ida}^{2-}$ ) bond with concomitant *mer*-chelating (*m*) conformation (**1**) of the coordinated  $\text{ida}^{2-}$  moiety, in contrast to the *fac*-chelating (*f*) conformation (**2**) of the coordinated  $\text{ida}^{2-}$  moiety in the

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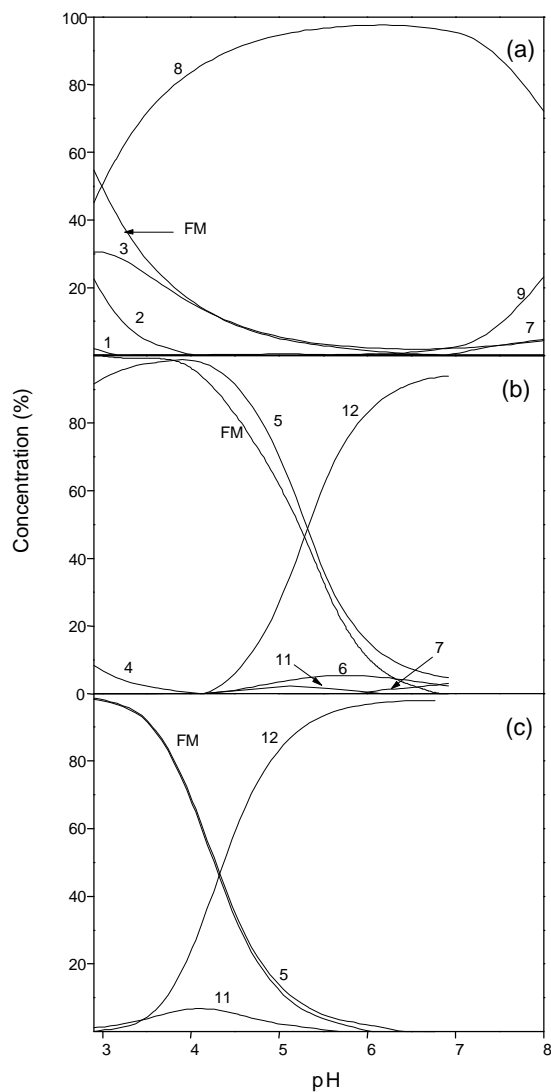
binary poly-[Cu(ida)(H<sub>2</sub>O)<sub>2</sub>] and in all 1:1:2 mixed ligand Cu<sup>II</sup>-ida<sup>2-</sup> (or ida<sup>2-</sup> like)/N-heterocyclic base complexes.<sup>12,13</sup>



The present equilibrium study of the mixed ligand complex formation of copper(II) with ida<sup>2-</sup> and two heterocyclic N-bases, viz., imidazole (imz) and benzimidazole (bz) (B) in 1:1:1 and 2:2:1 molar proportions in aqueous solution at fixed ionic strength,  $I = 0.1 \text{ mol dm}^{-3}$  (NaNO<sub>3</sub>) at  $25 \pm 1^\circ$  for determining the stability constants of binary Cu<sup>II</sup>-ida<sup>2-</sup>, Cu<sup>II</sup>-(B) and ternary Cu<sup>II</sup>-ida<sup>2-</sup>-(B) complexes is aimed at elucidating the *fac-mer* equilibria of the coordinated ida<sup>2-</sup> ligand in the formation of mixed ligand ternary Cu<sup>II</sup>-ida<sup>2-</sup>-B complexes out of the corresponding binary complexes.

## 2. Experimental

Iminodiacetic acid, imidazole, benzimidazole and all the other reagents were of AR grade. The solutions for potentiometric pH measurements and spectral studies were prepared in double distilled CO<sub>2</sub>-free water. Copper (II) nitrate solution was prepared by dissolving freshly precipitated alkali free Cu(OH)<sub>2</sub> in AR grade nitric acid and was standardised by use of a combination of ion-exchange method, acid-base and complexometric titrations.<sup>14</sup> pH measurements were carried out with Systronics digital pH-meter, type-335 (accuracy  $\pm 0.01$  pH) using a special glass electrode (pH 1–14) in conjunction with a saturated calomel electrode. Electronic spectral measurements were carried out with Hitachi U-3501 spectrophotometer. Equilibrium study for the determination of formation constants of Cu<sup>II</sup>-ida<sup>2-</sup>-B complexes involved pH-metric titrations of a series of solutions, each of initial volume 0.025 dm<sup>3</sup>, containing known amounts (0.001–0.002 mol dm<sup>-3</sup>) of iminodiacetic acid and/or B (imz and bz) in their protonated forms (ida H<sub>3</sub><sup>+</sup> and/or BH<sub>2</sub><sup>2+</sup>) containing known amounts (0.005 mol dm<sup>-3</sup>) of free HNO<sub>3</sub> in the absence and in the presence of known amounts (0.001–0.002 mol dm<sup>-3</sup>) of Cu<sup>II</sup>-nitrate with a carbonate-free<sup>15</sup> standard 0.1 mol dm<sup>-3</sup> solution of NaOH, maintaining a fixed ionic strength,  $I = 0.1 \text{ mol dm}^{-3}$  (NaNO<sub>3</sub>) at  $25 \pm 1^\circ$  (thermostated). pH-volume (of NaOH) data that were the averages of three titrations were accepted for calculating the formation constants using the computer program, SCOGS,<sup>16</sup> and the values of the constants giving minimum standard deviations were accepted. Complex formation equilibria were elucidated from analysis of the speciation curves (figures 1–3) obtained as computer outputs. Preliminary values of some of the constants supplied to the computer as input data were calculated according the method of Irving and Rossotti.<sup>17</sup> Ionic product

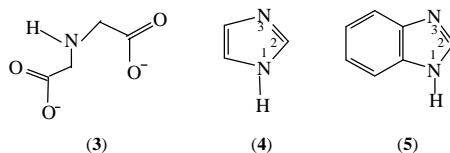


**Figure 1.** Speciation curves of (1:1) binary (a)  $\text{Cu}^{\text{II}}:\text{ida}^{2-}$ , (b)  $\text{Cu}^{\text{II}}:\text{imz}$  and (c)  $\text{Cu}^{\text{II}}:\text{bz}$  systems; (1)  $\text{idaH}_3^+$ , (2)  $\text{idaH}_2$ , (3)  $\text{idaH}^+$ , (4)  $\text{BH}_2^{2+}$ , (5)  $\text{BH}^+$ , (6)  $\text{Cu}(\text{OH})^+$ , (7)  $\text{Cu}(\text{OH})_2$ , (8)  $\text{Cu}(\text{ida})$ , (9)  $\text{Cu}(\text{ida})(\text{OH})^-$ , (11)  $\text{Cu}(\text{B})^{2+}$ , (12)  $\text{Cu}(\text{H}_1\text{B})^+$ , FM = free  $\text{Cu}^{\text{II}}$ .

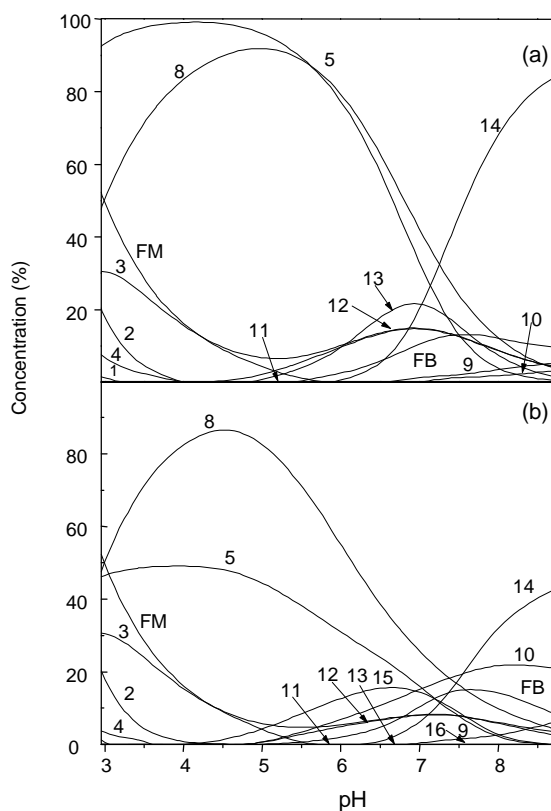
of water at the experimental temperature and the activity coefficient of hydrogen ion at the experimental ionic strength were obtained from the literature.<sup>18,19</sup> Analytical concentrations of  $\text{H}^+$  ion at different pH-meter readings were calculated by following the usual procedure.<sup>20</sup>

### 3. Results and discussion

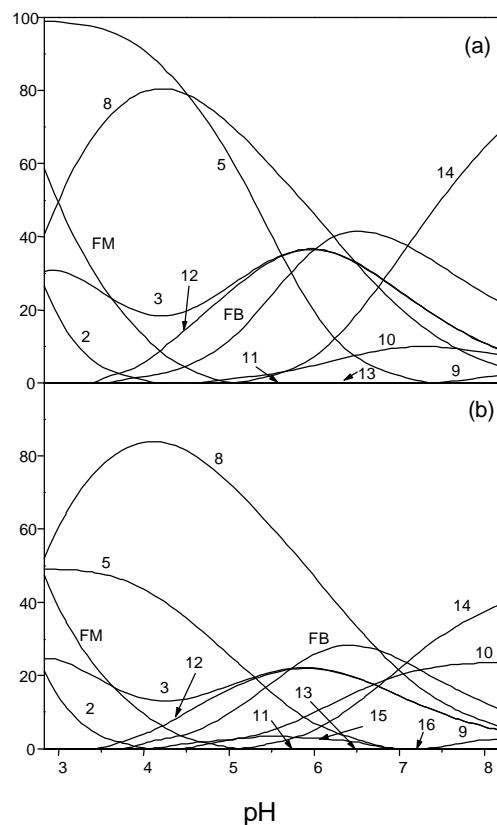
Protonated iminodiacetic acid ( $\text{idaH}_3^+$ ) titrates as a biprotic acid in the pH range 2–4 due to successive deprotonation of its two carboxylic acid groups. It shows another buffer region in the pH range 8–10 due to ionisation of the iminium proton. The iminodiacetate dianion ( $\text{ida}^{2-}$ , **3**) coordinates as a ( $\text{O}^-$ , N,  $\text{O}^-$ ) terdentate ligand<sup>11–13</sup>. Imidazole (imz, **4**)



and benzimidazole (bz, **5**) exist in their protonated forms in the pH range 2–5 and coordinate as monodentate ligands using their  $\text{N}_3$ -heteroatoms.<sup>10</sup>



**Figure 2.** Speciation curves of ternary  $\text{Cu}^{\text{II}}:\text{ida}^{2-}:\text{imz}$  systems: (a) 1:1:1 and (b) 2:2:1; (1)  $\text{idaH}_3^+$ , (2)  $\text{idaH}_2$ , (3)  $\text{idaH}^+$ , (4)  $\text{imzH}_2^{2+}$ , (5)  $\text{imzH}^+$ , (6)  $\text{Cu}(\text{OH})^+$ , (7)  $\text{Cu}(\text{OH})_2$ , (8)  $\text{Cu}(\text{ida})$ , (9)  $\text{Cu}(\text{ida})(\text{OH})^-$ , (10)  $(\text{ida})\text{Cu}(\text{OH})\text{Cu}(\text{ida})^-$ , (11)  $\text{Cu}(\text{imz})^{2+}$ , (12)  $\text{Cu}(\text{H}_1\text{imz})^+$ , (13)  $\text{Cu}(\text{ida})(\text{imz})$ , (14)  $\text{Cu}(\text{ida})(\text{H}_1\text{imz})^-$ , (15)  $\text{Cu}_2(\text{ida})_2(\text{imz})$ , (16)  $\text{Cu}_2(\text{ida})_2(\text{H}_1\text{imz})^-$ , FM = free  $\text{Cu}^{\text{II}}$ , FB = free imz.



**Figure 3.** Speciation curves of Cu<sup>II</sup>:ida<sup>2-</sup>:bz systems: (a) 1:1:1 and (b) 2:2:1; (1) idaH<sub>3</sub><sup>+</sup>, (2) idaH<sub>2</sub>, (3) idaH<sup>-</sup>, (4) bzH<sub>2</sub><sup>2+</sup>, (5) bzH<sup>+</sup>, (6) Cu(OH)<sup>+</sup>, (7) Cu(OH)<sub>2</sub>, (8) Cu(ida), (9) Cu(ida)(OH)<sup>-</sup>, (10) (ida)Cu(OH)Cu(ida)<sup>-</sup>, (11) Cu(bz)<sup>2+</sup>, (12) Cu(H<sub>1</sub>bz)<sup>+</sup>, (13) Cu(ida)(bz), (14) Cu(ida)(H<sub>1</sub>bz)<sup>-</sup>, (15) Cu<sub>2</sub>(ida)<sub>2</sub>(bz), (16) Cu<sub>2</sub>(ida)<sub>2</sub>(H<sub>1</sub>bz)<sup>-</sup>, FM = free Cu<sup>II</sup>, FB = free bz.

### 3.1 Cu<sup>II</sup>:ida<sup>2-</sup> equilibria

In the binary Cu<sup>II</sup>-ida<sup>2-</sup> systems, the Cu(ida) complex forms ~40% of total Cu<sup>II</sup> even at pH value as low as 2 but it exceeds 95% in the pH range 6–7. The predominant complex formation equilibria in the pH range 2–7, as the speciation curves (figure 1a) imply, are the following:



Cu<sup>II</sup> in the binary Cu(ida) complex is coordinated by the two carboxylate O-atoms on the equatorial plane. The imino N-atom however coordinates axially giving a *fac*-chelating conformation (2) to the coordinately unsaturated Cu(ida) complex, which takes up two

molecules of solvent H<sub>2</sub>O as additional ligands and exists in an asymmetrically elongated octahedral structure having two nearly perpendicular 5-membered chelate rings, providing two of the four closest Cu<sup>II</sup> donors plus another distant axial carboxylate O-donor to the metal ion. Single crystal X-ray diffraction study<sup>11</sup> on poly-[Cu(ida)(H<sub>2</sub>O)<sub>2</sub>] shows that, of the two H<sub>2</sub>O ligands coordinated to Cu<sup>II</sup> in the distorted octahedral geometry of this complex, one is more strongly bonded to Cu<sup>II</sup>,  $d(\text{Cu}-\text{OH}_2) = 1.976 \text{ \AA}$ , than the other,  $d(\text{Cu}^{\text{II}}-\text{OH}_2) = 2.378 \text{ \AA}$ . With rise of pH above 7, the Cu(ida) complex shows another buffer region, liberating one mole of H<sup>+</sup> per Cu<sup>II</sup>, obviously due to deprotonation of the more strongly coordinated H<sub>2</sub>O ligand to produce the ternary hydroxo complex, Cu(ida)(OH)<sup>-</sup> according to,

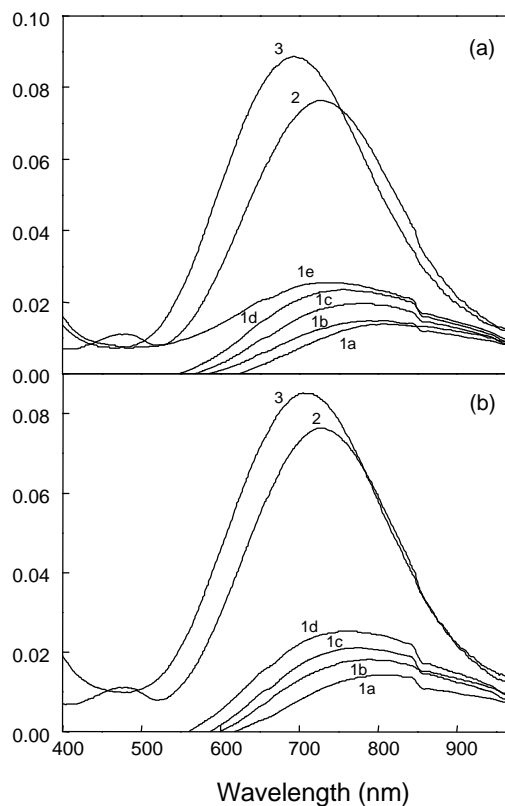


### 3.2 Binary Cu<sup>II</sup>:B equilibria (B = imz, bz)

In pH range 3.5 to 7, Cu(H<sub>1</sub>B)<sup>+</sup> species (B = imidazole, benzimidazole) are formed through coordination of N<sub>1</sub> of B with deprotonation of the pyrrole type N<sub>1</sub>-H group. Electronic spectroscopic evidence supports the formation of these species. Absorption maxima of 1:1 Cu<sup>2+</sup>:B mixtures in the pH range 3.5 to 7 show continuous blue shift with increase of pH (table 1 and figure 4). Such metal ion induced deprotonations of the coordinated imidazolyl N<sub>1</sub>-H group have been reported for the Cu<sup>II</sup>-complexes containing histidine residues. Coordination of a negatively charged heterocyclic-N donor generally results in a blue shift of absorption maxima due to stronger crystal field provided by it as compared to an uncharged heterocyclic-N donor. In the present study, distinct blue shifts

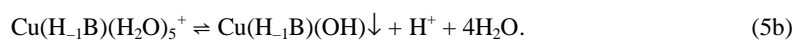
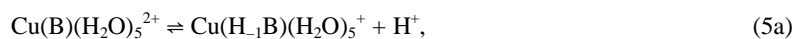
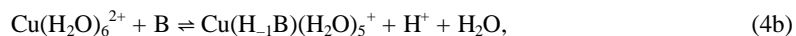
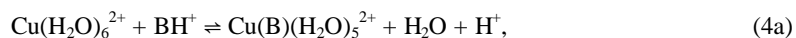
**Table 1.** Absorption maxima of Cu<sup>II</sup> in 1:1 Cu<sup>II</sup>:B mixtures at different pH values and those of 1:1 Cu<sup>II</sup>:ida<sup>2-</sup> 1:1:1 Cu<sup>II</sup>:ida<sup>2-</sup>:B mixtures at the pH values of maximum formation of Cu(ida), Cu(ida)(H<sub>1</sub>B)<sup>-</sup> complexes, where, B = imz, bz; [Cu<sup>II</sup>] = [ida] = [B] = 0.001 mol dm<sup>-3</sup> in aqueous solution, ionic strength  $I = 0.1 \text{ mol dm}^{-3}$  (NaNO<sub>3</sub>), optical path length = 1 cm.

Composition		pH	$I_{\text{max}}$ (nm)	(e)
Cu <sup>II</sup> -imz	(1:1)	3.00	816	11.1
		4.00	808	14.0
		5.00	804	14.4
		6.00	787	15.3
		6.25	781	19.6
		6.50	758	23.6
		6.75	729	25.5
Cu <sup>II</sup> -bz	(1:1)	3.00	808	11.0
		4.00	807	12.0
		5.00	805	14.2
		6.00	791	18.2
		6.25	778	21.1
		6.50	754	25.4
Cu <sup>II</sup> -ida	(1:1)	6.50	723	76.4
Cu <sup>II</sup> -ida-imz	(1:1:1)	8.00	693	88.9
Cu <sup>II</sup> -ida-bz	(1:1:1)	8.00	705	85.2



**Figure 4.** Superimposed electronic spectral curves of Cu<sup>II</sup>-ida<sup>2-</sup>-B systems: (a) B = imz, (b) B = bz; (1) 1 : 1 Cu<sup>II</sup>-B: 1a. pH 5, 1b. pH 6, 1c. pH 6.25, 1d. pH 6.5, 1e. pH 6.75, (2) 1 : 1 Cu<sup>II</sup>-ida<sup>2-</sup>, (3) 1 : 1 : 1 Cu<sup>II</sup>:ida<sup>2-</sup>:B mixtures at the pH of maximum formation of the respective complexes (table 1, figures 1-3).

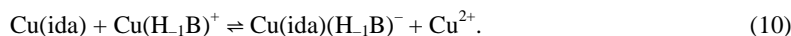
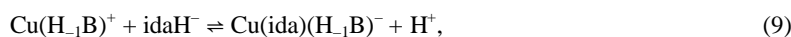
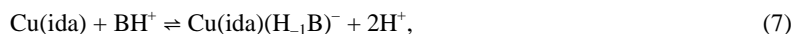
of absorption maxima in going from pH 5 to 7 for the Cu<sup>II</sup>-complexes of both imidazole and benzimidazole ligands strongly suggests deprotonation of the N<sub>1</sub>-H groups of the coordinated ligands and rules out the possibility of ionization of a coordinated H<sub>2</sub>O molecule, which usually results in small red shifts.<sup>21,22</sup> The spectral changes occurring between pH 3.5 to 7 may, therefore, be explained according to following equilibria:



At pH > 6, these  $\text{Cu}(\text{H}_1\text{B})^+$  complexes form >95% of total  $\text{Cu}^{\text{II}}$  in the binary 1:1  $\text{Cu}^{\text{II}} : \text{B}$  systems as the speciation curves (figures 1b, 1c) imply.

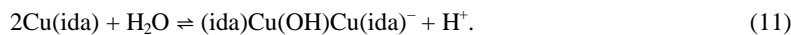
### 3.3 $\text{Cu}^{\text{II}} : \text{ida}^{2-} : \text{B}$ (imz, bz) equilibria

The early stages of complex formation in both the 1:1:1  $\text{Cu}^{\text{II}}\text{-ida}^{2-}\text{-B}$  systems (B = imz, bz) are dominated by the binary  $\text{Cu}(\text{ida})$  complex. Binary  $\text{Cu}(\text{B})^{2+}$  complexes are practically nonexistent in these systems. However,  $\text{Cu}(\text{H}_1\text{B})^+$  complexes form ~20–40% of the total  $\text{Cu}^{\text{II}}$  in the pH range 5–7. Mixed ligand  $\text{Cu}^{\text{II}}\text{-ida}^{2-}\text{-B}$  complexes appear at pH > 5 according to the equilibria (6–10) as the speciation curves (figures 2a, 3a) imply:



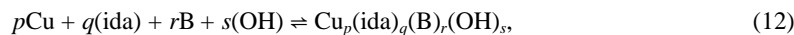
Small amounts of the ternary hydroxo complex,  $\text{Cu}(\text{ida})(\text{OH})^-$ , also appears above pH 7 according to equilibrium (3). The ternary  $\text{Cu}(\text{ida})(\text{imz})$  complex contributes ~20% of total  $\text{Cu}^{\text{II}}$  at pH 6.5–7.5, but the corresponding complex with bz is not identifiable on the speciation curves. This shows a higher tendency of imz over bz to form mixed ligand complexes. However the  $\text{B}(\text{N}_1\text{-H})$  deprotonated ternary complexes,  $\text{Cu}(\text{ida})(\text{H}_1\text{B})^-$ , occur as dominant mixed ligand species at pH > 7 in both these ternary systems.

Computer simulation of pH titration data of the 2:2:1  $\text{Cu}^{\text{II}} : \text{ida}^{2-} : \text{B}$  systems (figures 2b, 3b) indicate the formation of small amounts (~5–10%) of imidazole-bridged or benzimidazole-bridged binuclear complexes  $(\text{ida})\text{Cu}(\text{B})\text{Cu}(\text{ida})$ , trace amounts of  $(\text{ida})\text{Cu}(\text{H}_1\text{B})\text{Cu}(\text{ida})^-$  and a hydroxo bridged binuclear complex,  $(\text{ida})\text{Cu}(\text{OH})\text{Cu}(\text{ida})^-$ . Inclusion of oxo-bridged, oxo-hydroxo bridged and/or, dioxo-bridged binuclear complexes in the calculations gives higher values of the standard deviations. The ternary  $\text{Cu}(\text{ida})(\text{H}_1\text{B})^-$  complexes and the hydroxo-bridged binuclear  $(\text{ida})\text{Cu}(\text{OH})\text{Cu}(\text{ida})^-$  complex are the major  $\text{Cu}^{\text{II}}$ -containing species in these systems at pH > 7. As the speciation curves (figures 2, 3) imply, the  $(\text{ida})\text{Cu}(\text{OH})\text{Cu}(\text{ida})^-$  complex, is formed according to,



### 3.4 Calculation of the formation constants

The overall formation constants ( $\mathbf{b}_{pqrs}$ ) of the complexes may be defined according to,





$$\mathbf{b}_{pqrs} = \frac{[\text{Cu}_p(\text{ida})_q(\text{B})_r(\text{OH})_s]}{[\text{Cu}]^p[\text{ida}]^q[\text{B}]^r[\text{OH}]^s}, \quad (12a)$$

where, the stoichiometric numbers  $p$ ,  $q$  and  $r$  may be positive integers or zero;  $s$  is a negative integer for a protonated species, positive integer for a deprotonated, or a hydroxo-, or an oxo-species and zero for a normal species. Charges are not shown in the expressions for clarity.  $\mathbf{b}_{pqrs}$  values may be obtained directly as computer output, from which the individual step formation constants may be calculated using the following relations:

$$\log K_{\text{Cu}+\text{idaH}_2}^{2\text{H}} = \log \mathbf{b}_{1100} + \log K_{\text{idaH}_2}^{2\text{H}}, \quad (1a)$$

$$\log K_{\text{Cu}+\text{idaH}}^{\text{H}} = \log \mathbf{b}_{1100} + \log K_{\text{idaH}}^{\text{H}}, \quad (2a)$$

$$\log K_{\text{Cu}(\text{ida})}^{\text{H}} = \log \mathbf{b}_{1101} - \log \mathbf{b}_{1100}, \quad (3a)$$

$$\log K_{\text{Cu}(\text{ida})+\text{BH}}^{\text{H}} = \log \mathbf{b}_{1110} - \log \mathbf{b}_{1100} + \log K_{\text{BH}}^{\text{H}}, \quad (6a)$$

$$\log K_{\text{Cu}(\text{ida})+\text{BH}}^{2\text{H}} = \log \mathbf{b}_{1111} - \log \mathbf{b}_{1100} + \log K_{\text{BH}}^{\text{H}}, \quad (7a)$$

$$\log K_{\text{Cu}(\text{ida})+\text{B}}^{\text{H}} = \log \mathbf{b}_{1111} - \log \mathbf{b}_{1100}, \quad (8a)$$

$$\log K_{\text{Cu}(\text{H}_{-1}\text{B})+\text{idaH}}^{\text{H}} = \log \mathbf{b}_{1111} - \log \mathbf{b}_{1011} + \log K_{\text{idaH}}^{\text{H}}, \quad (9a)$$

$$\log K_{2\text{Cu}(\text{ida})}^{\text{H}} = \log \mathbf{b}_{2201} - 2 \log \mathbf{b}_{1100}, \quad (11a)$$

where,  $\mathbf{b}_{1100}$ ,  $\mathbf{b}_{1101}$ ,  $\mathbf{b}_{1011}$ ,  $\mathbf{b}_{1110}$ ,  $\mathbf{b}_{1111}$  and  $\mathbf{b}_{2201}$  are the overall formation constants of  $\text{Cu}(\text{ida})$ ,  $\text{Cu}(\text{ida})(\text{OH})^-$ ,  $\text{Cu}(\text{H}_{-1}\text{B})^-$ ,  $\text{Cu}(\text{ida})(\text{B})$ ,  $\text{Cu}(\text{ida})(\text{H}_{-1}\text{B})^-$  and  $(\text{ida})\text{Cu}(\text{OH})\text{Cu}(\text{ida})^-$  complexes respectively.

### 3.5 Fac-mer equilibrium of coordinated $\text{ida}^{2-}$

Despite the fact that the ternary  $\text{Cu}(\text{ida})(\text{H}_{-1}\text{B})^-$  complexes form ~ (70–80)% of the total  $\text{Cu}^{\text{II}}$  at  $\text{pH} > 7$ , the experimental values of  $\Delta \log K_{\text{Cu}}$ ,<sup>23</sup> corresponding to the repropor-tionation equilibria (10), defined according to,

$$10^{(\Delta \log K_{\text{Cu}})_{\text{expt}}} = \frac{[\text{Cu}(\text{ida})(\text{H}_{-1}\text{B})][\text{Cu}]}{[\text{Cu}(\text{ida})][\text{Cu}(\text{H}_{-1}\text{B})]}, \quad (10a)$$

and calculated using the relation,

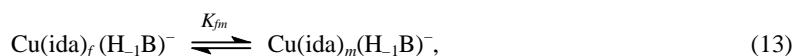
$$(\Delta \log K_{\text{Cu}})_{\text{expt}} = \log \mathbf{b}_{\text{Cu}(\text{ida})(\text{H}_{-1}\text{B})}^{\text{Cu}} - \log K_{\text{Cu}(\text{ida})}^{\text{Cu}} - \log K_{\text{Cu}(\text{H}_{-1}\text{B})}^{\text{Cu}}, \quad (10b)$$

are not favourable (table 2). This may be attributed to the change in the mode of coordination of the ( $O^-$ , N,  $O^-$ ) terdentate  $ida^{2-}$  ligand from the *fac*-chelating (*f*) mode (2)

**Table 2.** Stability constants and other related constants of binary  $Cu^{II}$ - $ida^{2-}$ ,  $Cu^{II}$ -B and ternary  $Cu^{II}$ - $ida^{2-}$ -B complexes (B = imz, bz) at  $25 \pm 1^\circ$  in aqueous solution, ionic strength,  $I = 0.1 \text{ mol dm}^{-3}$  ( $NaNO_3$ ). Stoichiometric numbers,  $p$ ,  $q$ ,  $r$ ,  $s$  and eqm. numbers are shown in the parentheses.

(a) Protonation constants of the ligands					
		$ida^{2-}$		imz	bz
$pK_3^H$	(010-3)	1.80		-	-
$pK_2^H$	(010-2)	2.77	(001-2)	1.86	(001-2) 0.30
$pK_1^H$	(010-1)	9.40	(001-1)	7.50	(001-1) 5.73
(b) $Cu^{II}$ - $ida^{2-}$ constants					
$\log K_{Cu(ida)}^{Cu}$	(1100)	$\log b_{Cu(ida)(OH)}^{Cu}$	(1101)	$\log b_{Cu_2(ida)_2(OH)}^{Cu}$	(2201)
	9.95		1.39		16.29
(c) $Cu^{II}$ -B constants (B = imz, bz)					
				imz	bz
$\log K_{Cu(B)}^{Cu}$	(1010)			5.85	3.90
$\log K_{Cu(H_{-1}B)}^{Cu}$	(1011)			0.25	0.45
$Cu$ - $ida^{2-}$ -B constants					
				imz	bz
$\log b_{Cu(ida)(B)}^{Cu}$	(1110)			13.68	10.55
$(\Delta \log K_{Cu})_{\text{expt}}$				-2.12	-3.30
$\log b_{Cu(ida)(H_{-1}B)}^{Cu}$	(1111)			6.65	6.62
$(\Delta \log K_{Cu})_{\text{expt}}$				-3.25	-3.78
$\log b_{Cu_2(ida)_2B}^{Cu}$	(2210)			27.83	24.40
$\log b_{Cu_2(ida)_2(H_{-1}B)}^{Cu}$	(2211)			18.83	15.40
(e) Stepwise formation constants					
		$ida^{2-}$		imz	bz
$\log K_{Cu+idaH_2}^{2H}$	(1a)	-2.22		-	-
$\log K_{Cu+idaH}^H$	(2a)	0.55		-	-
$\log K_{Cu(ida)}^H$	(3a)	-6.15		-	-
$\log K_{Cu(ida)+BH}^H$	(6a)	-		-3.77	-5.13
$\log K_{Cu(ida)+BH}^{2H}$	(7a)	-		-10.80	-9.06
$\log K_{Cu(ida)+B}^H$	(8a)	-		-3.30	-3.33
$\log K_{fm}$	(13c)	-		-3.25	-3.48
$\log K_{Cu(H_{-1}B)+idaH}^H$	(9a)	-		-3.00	-3.23

in the binary Cu(ida) complex to the *mer*-chelating (*m*) mode (1) in the ternary Cu(ida)(H<sub>1</sub>B)<sup>-</sup> complexes according to,



as the B ligands coordinate with the binary Cu(ida)<sub>f</sub> complex to form the ternary Cu(ida)<sub>m</sub>(H<sub>1</sub>B)<sup>-</sup> complexes. The *fac-mer* equilibrium constant, *K<sub>fm</sub>*, may be defined as,

$$K_{fm} = \frac{10^{(\Delta \log K_{\text{Cu}})_{\text{expt}}}}{10^{(\Delta \log K_{\text{Cu}})_{\text{stat}}}}, \quad (13a)$$

where, (Δlog*K<sub>Cu</sub>*)<sub>stat</sub> corresponds to the reproporationation equilibria (10) not involving the *fac-mer* equilibria (13) and (Δlog*K<sub>Cu</sub>*)<sub>expt</sub> corresponds to the same equilibrium involving the *fac-mer* equilibria (13). Thus,

$$\log K_{fm} = (\Delta \log K_{\text{Cu}})_{\text{expt}} - (\Delta \log K_{\text{Cu}})_{\text{stat}}. \quad (13b)$$

Considering *fac*-mode (*f*) of coordination of ida<sup>2-</sup> in Cu(ida) and *mer*-mode (*m*) of coordination of ida<sup>2-</sup> in Cu(ida)(H<sub>1</sub>B)<sup>-</sup>, one may obtain log*K<sub>fm</sub>* from (10b) and (13b) as,

$$\log K_{fm} = \log b_{\text{Cu(ida)}_m(\text{H}_{-1}\text{B})}^{\text{Cu}} - \log K_{\text{Cu(ida)}_f}^{\text{Cu}} - \log K_{\text{Cu(H}_{-1}\text{B})}^{\text{Cu}} - (\Delta \log K_{\text{Cu}})_{\text{stat}}. \quad (13c)$$

The statistical value of Δlog*K<sub>Cu</sub>*, i.e. (Δlog*K<sub>Cu</sub>*)<sub>stat</sub> for the ternary Cu(ida)<sub>f</sub>(H<sub>1</sub>B)<sup>-</sup> complexes may be calculated by comparing the coordination tendency of the monodentate (H<sub>1</sub>B)<sup>-</sup> ligand species to a (O<sup>-</sup>, N, O<sup>-</sup>) terdentate *fac*-chelated distorted octahedral Cu(ida)<sub>f</sub> complex relative to an octahedral Cu<sup>II</sup> (*aq*) ion using the relation,

$$(\Delta \log K_{\text{Cu}})_{\text{stat}} = \log K_{\text{Cu(ida)}_f(\text{H}_{-1}\text{B})}^{\text{Cu(ida)}_f} - \log K_{\text{Cu(H}_{-1}\text{B})}^{\text{Cu}}. \quad (14)$$

A monodentate (H<sub>1</sub>B)<sup>-</sup> ligand can be associated to a (O<sup>-</sup>, N, O<sup>-</sup>) terdentate *fac*-chelated distorted octahedral complex in three different ways and the resulting ternary complex, Cu(ida)<sub>f</sub>(H<sub>1</sub>B)<sup>-</sup>, can give up the (H<sub>1</sub>B)<sup>-</sup> ligand only in one way. Again, a monodentate (H<sub>1</sub>B)<sup>-</sup> ligand can coordinate an octahedral Cu<sup>II</sup>(*aq*) ion in six different ways, whereas, the resulting binary complex, Cu(H<sub>1</sub>B)<sup>+</sup>, can dissociate only in one way. Hence the stability of the ternary Cu(ida)<sub>f</sub>(H<sub>1</sub>B)<sup>-</sup> complexes relative to the binary Cu(H<sub>1</sub>B)<sup>+</sup> complexes will be given by the ratio of the corresponding step stability constants, which may be expressed in terms of the ratio of the relative probabilities of formation of the corresponding complexes as,

$$10^{(\Delta \log K_{\text{Cu}})_{\text{stat}}} = (K_{\text{Cu(ida)}_f(\text{H}_{-1}\text{B})}^{\text{Cu(ida)}_f}) / (K_{\text{Cu(H}_{-1}\text{B})}^{\text{Cu}}) = (3/1)/(6/1) = 1/2, \quad (14a)$$

which gives,

$$(\Delta \log K_{\text{Cu}})_{\text{stat}} = -0.3. \quad (14b)$$

Negative value of  $\log K_{fm}$  is the outcome of the structural change involving the rupture and formation of at least one of the two  $\text{Cu}^{\text{II}}\text{-O}$  bonds in the *fac* to *mer* transformation of the ( $\text{O}^-$ , N,  $\text{O}^-$ ) terdentate chelated  $\text{ida}^{2-}$  ligand ion in the  $\text{Cu}(\text{ida})$  complex.

### 3.6 Spectral evidence of *fac-mer* equilibria

The existence of *fac-mer* equilibria is also evident from the difference in the superimposed electronic spectral curves (figure 4) of the 1:1  $\text{Cu}^{\text{II}}:\text{ida}^{2-}$ , 1:1  $\text{Cu}^{\text{II}}:\text{B}$  and 1:1:1  $\text{Cu}^{\text{II}}:\text{ida}^{2-}:\text{B}$  mixtures at pH values corresponding to the maximum formation of the binary  $\text{Cu}(\text{ida})$ ,  $\text{Cu}(\text{H}_1\text{B})^+$  and ternary  $\text{Cu}(\text{ida})(\text{H}_1\text{B})^-$  complexes respectively (figures 1–3). As  $\text{Cu}(\text{ida})_f(\text{H}_1\text{B})^-$  is transformed to  $\text{Cu}(\text{ida})_m(\text{H}_1\text{B})^-$ , the coordination geometry of  $\text{Cu}^{\text{II}}$  changes from distorted octahedral in  $\text{Cu}(\text{ida})_f(\text{H}_1\text{B})^-$  to predominantly square pyramidal/square planar in  $\text{Cu}(\text{ida})_m(\text{H}_1\text{B})^-$ , in which the hetero N-atom of  $(\text{H}_1\text{B})^-$  is coordinated *trans*- to the imino N-atom of  $\text{ida}^{2-}$ , consequently the absorption maxima of  $\text{Cu}^{\text{II}}$  shows a blue shift of ~30 nm for  $\text{Cu}(\text{ida})_m(\text{H}_1\text{imz})^-$  and ~(15–20 nm) for  $\text{Cu}(\text{ida})_m(\text{H}_1\text{bz})^-$  complexes (table 1).

## 4. Conclusion

The combined pH-metric and spectrophotometric investigations of  $\text{Cu}^{\text{II}}\text{-ida}^{2-}\text{-B}$  (imz, bz) systems reveal that, between imidazole and benzimidazole, the former has a relatively stronger tendency to form mixed ligand  $\text{Cu}(\text{ida})(\text{H}_1\text{B})^-$  complexes. The coordinated  $\text{ida}^{2-}$  ligand in these  $\text{Cu}^{\text{II}}$  complexes undergoes a structural change from *fac*-mode (2) to *mer*-mode (1) as the binary  $\text{Cu}(\text{ida})_f$  complex is coordinated by the heterocyclic N-donor ligands, viz. imz and bz. Such alteration of the modes of coordination of a  $\text{Cu}^{\text{II}}$ -bonded  $\text{O}^-$ , N,  $\text{O}^-$  donor ligand due to coordination of heterocyclic N-bases to  $\text{Cu}^{\text{II}}$  is of great relevance to the changes of active site structures of many copper-proteins during their bio-functions.<sup>1,3,24,25</sup>

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