

# Mixed Ligand Complexes of Benzimidazole and Pyrimidine Hydroxy Azo Dyes with Some Transition Metals and Glycine, *DL*-Alanine, or *DL*-Leucine

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**Summary.** The overall formation constants of ternary complexes of Cu(II), Zn(II), and Cd(II) with glycine (*Gly*), *DL*-alanine (*Ala*), or *DL*-leucine (*Leu*) as primary and 2-(*o*-hydroxyphenylazo)-2-cyanomethyl benzimidazole (*ABI*) and 5-(*o*-hydroxyphenylazo) barbituric acid (*ABA*) as secondary ligands as well as those of the binary systems have been investigated potentiometrically in 40% (v/v) EtOH. The stability of the ternary complexes is compared quantitatively with that of the corresponding binary complexes. The concentration distribution of the species formed in solution was evaluated; they were characterized by means of IR and <sup>1</sup>H NMR spectroscopy.

**Keywords.** Amino acids; Azo dyes; Complexes.

## Ternäre Komplexe von Hydroxyphenylazoverbindungen mit einigen Übergangsmetallen und Glycin, *DL*-Alanin oder *DL*-Leucin

**Zusammenfassung.** Die Bildungskonstanten der ternären Komplexe von Cu(II), Zn(II) und Cd(II) mit Glycin (*Gly*), *DL*-Alanin (*Ala*) oder *DL*-Leucin (*Leu*) als Primärliganden und 2-(*o*-Hydroxyphenylazo)-2-cyanomethyl-benzimidazol (*ABI*) bzw. 5-(*o*-Hydroxyphenylazo)-barbitursäure (*ABA*) als Sekundärliganden wurden ebenso wie jene binärer Systeme potentiometrisch in 40% (v/v) Ethanol bestimmt. Die Stabilität der ternären Komplexe wird mit jener der binären verglichen. Die Konzentration der verschiedenen Spezies in Lösung sowie ihre IR- und <sup>1</sup>H-NMR-Spektren wurden gemessen.

## Introduction

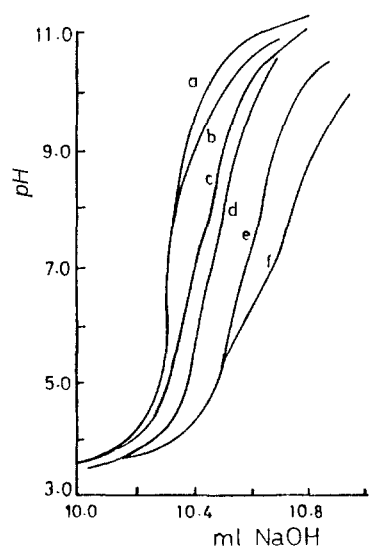
It has been shown that the arylazo derivatives of benzimidazole and barbituric acid play an important role in biochemistry [1–5]. Much attention has been paid recently to the study of ternary complexes of transition metals with molecules of biological and pharmaceutical interest [6–9]. Mixed complexes of transition metals containing an imidazole or pyrimidine group as ligands are commonly found in biological media and may play important roles in processes like catalysis of drug interaction with biomolecules [10, 11]. Furthermore, it has been suggested that the presence of metal ions in biological fluids could have a significant effect on the

therapeutic action of drugs [12, 13]. Literature data on the interaction of Cu(II), Zn(II), and Cd(II) with imidazole derivatives and amino acids demonstrate that the imidazole moiety is the principal site responsible for metal binding [10, 14, 15]. To obtain a better understanding of the driving forces leading to complexation in biological systems, we report here the results of *pH*-metric studies on the mixed ligand complexes of Cu(II), Zn(II), and Cd(II) with glycine (*Gly*), *DL*-alanine (*Ala*), and *DL*-Leucine (*Leu*) as primary ligands and 2-(*o*-hydroxyphenylazo)-2-cyanomethyl benzimidazole (*ABI*) and 5-(*o*-hydroxyphenylazo) barbituric acid (*ABA*) as secondary ligands. The work aims to establish the various equilibria existing in solution and to determine the dissociation constants of the free ligands and the stability constants of binary and ternary complexes in 40% (v/v) EtOH-H<sub>2</sub>O) at 37°C and *I* = 0.15 M NaClO<sub>4</sub>.

## Results and Discussion

### Proton-ligand systems

Representative *pH*-metric equilibrium titration curves for free and metal complexed ligands are depicted in Fig. 1. The acid dissociation constants of *ABI* and *ABA* in 40% (v/v) EtOH-H<sub>2</sub>O have been determined from curves *a* and *b* using a computer program based on the *Irving-Rossotti* equations [21]. Details regarding the potentiometric method are reported in the experimental section. The values of the dissociation constants of glycine, *DL*-alanine, and *DL*-leucine were also redetermined under the same experimental conditions (37°C, *I* = 0.15 M NaClO<sub>4</sub>). The SUPERQUAD computer program [22] was used to refine the overall protonation or formation constants. The *pK<sub>a</sub>* values obtained through refinement of several sets of potentiometric data are quoted in Table 1; they show good agreement with literature values taking into account changes in experimental conditions as well as in methods of calculation. It is worth mentioning that the *pK<sub>a1</sub>*



**Fig. 1.** Titration curves for Cu(II)-*Gly*-*ABA* (37°C, *I* = 0.15 M HClO<sub>4</sub>, 40% (v/v) EtOH); *a*: 0.02 M HClO<sub>4</sub>, *b*: *a* + 2 × 10<sup>-4</sup> M *Gly*, *c*: *b* + 1 × 10<sup>-4</sup> M Cu(II), *d*: *a* + 2 × 10<sup>-4</sup> M *ABA*, *e*: *d* + 1 × 10<sup>-4</sup> M Cu(II), *f*: *e* + 2 × 10<sup>-4</sup> M *Gly*; concentration of NaOH: 0.0825 mol·dm<sup>-3</sup>

**Table 1.** Ionisation constants of the free ligands and stability constants of binary systems (37°C,  $I = 0.15 M$  (NaClO<sub>4</sub>), error limit:  $\pm(0.02-0.06)$ )

Constants	<i>ABA</i>	<i>ABI</i>	<i>Gly</i>	<i>Ala</i>	<i>Leu</i>
H+					
$\log \beta_1$	7.27	8.02	–	–	–
$\log \beta_2$	16.43	19.35	9.45	9.72	9.58
Cu(II)					
$\log \beta_1$	5.65	5.52	7.97	7.74	7.66
$\log \beta_2$	10.63	10.27	14.88	14.42	14.02
Zn(II)					
$\log \beta_1$	5.22	5.03	5.48	5.36	5.24
$\log \beta_2$	9.47	9.07	10.03	10.00	9.60
Cd(II)					
$\log \beta_1$	5.04	4.85	5.13	5.09	4.21
$\log \beta_2$	8.90	8.64	9.35	9.42	7.62

values for amino acids appear too low ( $\leq 2.35$ , [23]) and exist only in strongly acidic solutions. Thus, these values have not been used in the calculations.

#### Binary metal-ligand systems

Analysis of curves *d* and *e* (Fig. 1) shows that the addition of metal ions to of solutions the free ligands shifts the buffer region of the ligand to lower *pH* values, indicating that the complexation reactions proceed by releasing of protons. Generally, it is observed that *MA* complexes (curve *c*) begin to form at lower *pH* ( $\sim 3.5$ ) than *MB* complexes (curve *e*,  $pH \geq 4.3$ ). The complexes are quite stable up to high *pH* values. Precipitation occurs at  $pH > 10.7$ ; thus, calculations have been performed beyond this point. Therefore, the hydroxo species likely to be formed after the precipitation point could not be investigated.

The present study shows that 1:1 and 1:2 metal:ligand species are the important types in both metal ion-amino acid (*A*) and azo ligand (*B*) systems. This result is based on the presence of two inflection points in the case of *MA* species and a single steep one in the case of *MB* after addition of two moles of NaOH per mole of ligand, indicating the dissociation of two protons from amino acids in a stepwise manner, whereas for *MB* systems a simultaneous complexation has to be accepted. The above equilibria can be represented as follows (charges are omitted for the sake of clarity):



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



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

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

$$\log K_{MB_2}^M = \log [MB_2] - ([\log [MB] + \log [B]) \quad (6)$$

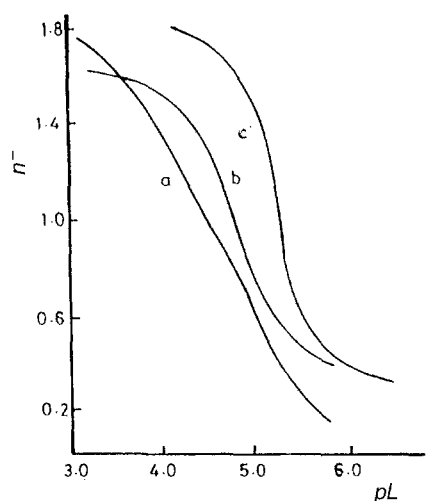


Fig. 2. Formation curves for metal ion – ABA binary systems; a: Cd(II), b: Zn(II), c: Cu(II)

The overall formation constants ( $\log \beta = \log K_{MA}^M + \log K_{MA_2}^{MA}$ ) are computed forms  $n^-$  vs.  $pL$  curves (Fig. 2) using standard procedures based on the calculation of the average number of ligands bound per metal ion ( $n^-$ ) and the free ligand exponent ( $pL$ ) as described previously [21]. The obtained values for  $\log \beta_1$  and  $\log \beta_2$  for different binary complexes are given in Table 1, limited to the range before the first formation of hydroxo complexes by the reasons discussed above. Other species were taken into consideration but were rejected during refinement because of their bad statistical data.

The data listed in Table 1 clearly reveal that the stabilities of metal – amino acid complexes are very close to those already published after allowing for changes in experimental conditions [10]. The results show that the stability order of binary systems in terms of amino acids is *Gly* > *Ala* > *Leu*. This trend does not follow the basicities as expected, probably because the  $pK$  values of the amino acids studied are so similar. It is suggested that the absence of an alkyl chain in *Gly* is responsible of the higher stability of its complex. Substitution by a  $\text{CH}_3$  groups (*Ala*) or lengthening of the skeleton (*Leu*) produces a small decrease in  $\log \beta$  values. In terms of the nature of metal ion, the complex stabilities follow the trend  $\text{Cu(II)} > \text{Zn(II)} > \text{Cd(II)}$ , which is in agreement with the decrease in ionic potential (charge/ionic radius). On the other hand, the results indicates that *MA* complexes are more stable than those of the *MB* type. This behaviour can be interpreted based on the bidentate nature of amino acids which coordinate through the amino nitrogen and the carboxylic oxygen atoms forming stable five-membered chelate ring. In contrast, the azo ligands *ABI* and *ABA* act as monobasic tridentate ligands, coordinated through the *o*-hydroxy oxygen, the azo nitrogen, and the  $\text{C}=\text{O}$  group of barbiturate or N-3 of benzimidazole leading to the formation of five or six-membered rings. It is well known that 3d metal ions prefer five-membered to six-membered rings during chelation [24].

#### Ternary metal-ligand systems

A set of typical titration curves for  $\text{Cu(II)-Gly}$ ,  $\text{Cu(II)-ABA}$ , and  $\text{Cu(II)-Gly-ABA}$  systems are shown in Fig. 1 (curve. f). Other mixed ligand systems with  $\text{Zn(II)}$  and

Cd(II) chelates show similar behaviour. In our study, the amino acids ( $A$ ) are considered as primary ligands and the azo compound ( $B$ ) as a secondary ligands since  $MA$  species are formed at lower  $pH$  values than  $MB$  species. The observed lowering of curve  $f$  in comparison to curves  $c$  and  $e$  (binary  $MA$  and  $MB$ ) indicates the formation of ternary complexes in solution. The best-fit computer models of the investigated ternary systems showed the sole presence of 1:1:1 species; other species were of very minor importance below  $pH$  6.0. Further, it is worth mentioning that these systems show no precipitation during titration. Thus, they do not hydrolyze under the experimental conditions, even at high  $pH$  values. This behaviour may be explained on the basis that the electron density of the metal-ligand bonds in ternary chelates is redistributed in such a way that the ternary chelates are more polar than the binary chelates.

Generally, the titration curves  $e$  and  $f$  (Fig. 1) overlap at low  $pH$  values; they diverge, however, at higher  $pH$ s. This suggests that the azo ligands do not participate in ternary systems at low  $pH$  values. Furthermore, the formation of mixed ligand chelates  $MAB$  is proved by the observation of an inflection point at  $m = 1$ , followed by a buffer region in the higher  $pH$  range ( $m$ : number of moles of alkali added per mol of metal ion). Up to this point, the  $MAB$  curve is almost coincident with the  $MA$  curve; beyond it, however, it runs much below the  $MA$  curve.

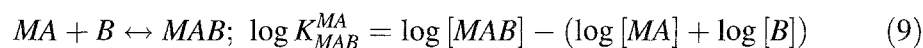
To discuss the stabilization of ternary chelates, two methods have been considered. In the first one the ternary complex formation is considered to take place in a simultaneous manner according to

$$\log \beta_{MAB}^M = \log [MAB] - (\log [M] + \log [A] + \log [B]) \quad (7)$$

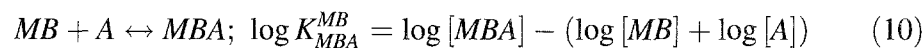
since  $\log [M] + \log [A] = \log [MA] - \log K_{MA}^M$  (Eq. (2)),

$$\log \beta_{MAB}^M = \log [MAB] - \log [MA] + \log K_{MA}^M + \log [B] \quad (8)$$

In the second method, the  $MAB$  chelate is considered to be formed in a stepwise manner, assuming that  $MA$  formed in the lower buffer region, followed by addition of the second ligand ( $B$ ) in the upper buffer region. This equilibrium can be represented as follows:



Similarly



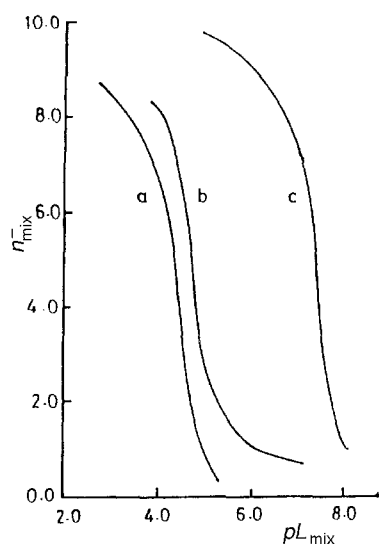
The experimentally determined  $\beta_{MAB}^{MB}$  is connected with  $K_{MAB}^{MA}$  and  $K_{MBA}^{MB}$  by the following equations:

$$\log \beta_{MAB}^M - \log K_{MA}^M = \log K_{MAB}^{MA} \quad (11)$$

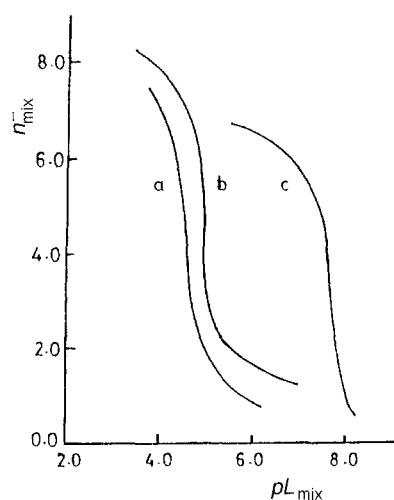
and

$$\log \beta_{MBA}^M - \log K_{MB}^M = \log K_{MBA}^{MB} \quad (12)$$

The average number of secondary ligand molecules associated with one mole of binary complex,  $n_{\text{mix}}^-$ , was computed. The resulting values were used for the calculation of the free secondary ligand exponent  $pL_{\text{mix}}$ . The formation constants



**Fig. 3.** Formation curves for metal ion-*Gly-ABA* ternary systems; *a*: Cd(II), *b*: Zn(II), *c*: Cu(II)



**Fig. 4.** Formation curves for metal ion-*Gly-ABI*; *a*: Cd(II), *b*: Zn(II), *c*: Cu(II)

of ternary systems were evaluated from the  $n_{\text{mix}}^-$  vs.  $pL_{\text{mix}}$  curves (Figs. 3 and 4). The results presented in Table 2 indicate that calculations based on Eq. (11) yield more reliable results than those on Eq. (12); thus, the ternary complex is formed simultaneously according to Eq. (7). This also confirms the assumption that the amino acids under investigation act as primary ligands in our ternary systems. Such observations are in line with those reported for ternary complexes of amines [25] and is contrary to earlier findings [26].

According to Sigel [6, 27], the relative stability of a ternary complex *MAB* as compared to its corresponding binary complex *MB* can be quantitatively expressed by the following equation:

$$\Delta \log K_M = \log \beta_{MAB} - (\log K_{MA} + \log K_{MB}) \quad (13)$$

A comparison of stability constants of binary complexes (Table 1) indicates that  $K_1 > K_2$ . Thus, in binary systems  $\Delta \log K$  values are generally negative which

**Table 2.** Stability Constants of  $M^{2+}$ -amino acid- azo dye ternary systems at 37°C

Metal ion	$\log \beta_{MAB}^M$	$\log K_{MAB}^{MA}$	$\log K_{MBA}^{MB}$	$\Delta \log X$	$\log X$	$\log X'$	$\log \beta_{stat}$
<i>M<sup>2+</sup>-Gly-ABA</i>							
Cu(II)	13.07	5.10	7.42	0.55	0.63	0.51	13.03
Zn(II)	10.00	4.52	4.78	0.70	0.50	0.23	9.78
Cd(II)	9.43	4.30	4.39	0.74	0.61	0.17	9.40
<i>M<sup>2+</sup>-Gly-ABI</i>							
Cu(II)	12.93	4.96	7.41	0.56	0.71	0.50	12.86
Zn(II)	9.89	4.41	4.86	0.62	0.68	0.31	9.84
Cd(II)	9.38	4.25	4.53	0.60	0.77	0.21	9.26
<i>M<sup>2+</sup>-Ala-ABA</i>							
Cu(II)	12.81	5.07	7.16	0.58	0.57	0.48	12.81
Zn(II)	10.06	4.70	4.84	0.52	0.65	0.17	10.01
Cd(II)	9.46	4.37	4.32	0.67	0.60	0.08	9.42
<i>M<sup>2+</sup>-Ala-ABI</i>							
Cu(II)	12.63	4.89	7.11	0.63	0.57	0.33	12.60
Zn(II)	9.85	4.49	4.82	0.54	0.63	0.18	9.81
Cd(II)	9.36	4.27	4.51	0.58	0.66	0.18	9.31
<i>M<sup>2+</sup>-Leu-ABA</i>							
Cu(II)	12.66	5.10	6.11	0.55	0.67	0.65	12.52
Zn(II)	9.88	4.64	4.66	0.58	0.69	0.30	9.78
Cd(II)	8.62	4.41	3.58	0.63	0.72	0.17	8.53
<i>M<sup>2+</sup>-Leu-ABI</i>							
Cu(II)	12.54	4.88	7.02	0.64	0.79	0.66	12.45
Zn(II)	9.63	4.39	4.20	0.64	0.59	0.24	12.60
Cd(II)	8.47	4.26	3.62	0.59	0.68	0.21	8.42

indicates the formation of 1:2 species. Similarly, in case of ternary complexes formation  $\Delta \log K$  should display the same trend. This behaviour can be explained on the basis of the presence of a fewer number of coordination sites on the  $MA$  monocomplexes than on the aquated metal ion. Thus, the secondary ligands ( $B$ ) are expected to bind the  $MA$  complex with a smaller stability constant than that with an aquated metal ion. Therefore,  $\Delta \log K$  should be negative, generally between  $-0.5$  and  $-2.0$  [6, 28] depending on the geometry of the complex. A positive or less negative  $\Delta \log K$  value indicates a significant stabilization of the ternary system. The quantitative stabilization of ternary complexes can also be expressed in terms of their disproportionation constant  $X$  [29, 30] as defined by Eq. (14):

$$\log X = 2 \log \beta_{MAB}^M - (\log \beta_{MA_2}^M + \log \beta_{MB_2}) \quad (14)$$

The values for  $\log X$  expected from statistical reasons is  $+0.6$  [30] for all geometries. More positive values than those expected statistically indicate marked stabilities of ternary complexes. Further,  $\log X$  values can only indicate the coordination tendency of secondary ligand towards  $MA$ , but it fail to throw any light on the stabilizing order of metal-ligand bonds after the ternary complex formation. Hence, to discuss the new stabilization constant  $\log X'$ , the following

equation has been considered:

$$\Delta \log X' = (\log \beta_{MAB}^M + \log K_{MA}^M) - (\log \beta_{MA_2} + \log K_{MB}^M) \quad (15)$$

The computed values for  $\Delta \log K$ ,  $\log X$ , and  $\log X'$  for various ternary system are listed in Table 2. Some general observation about the behaviour of the various systems are discussed in the following.

(a) The  $\Delta \log K$  values obtained for the above ternary systems generally do not deviate from the statistical expectations [27] where the statistical, steric, and electrostatic factors result in lower stability constants for the ternary complexes as compared to the corresponding binary systems. The absence of stabilization is compatible with the explanations given by *Sigel et al.* [31–33] for the possible stabilization of ternary complexes. The data indicate that the  $\Delta \log K$  values obtained for *M-Gly-B* are more positive than the values obtained for *M-Ala-B*, indicating a marked stability of *M-Gly-B*. This is due to the limited tendency of alanine for interligand interaction [34], whereas glycine complexes sometimes exhibit exceptional stability [35]. Based on the fact that  $\Delta \log K$  depends on the coordination numbers of metal ion and ligands [36, 37], the change in  $\Delta \log K$  values obtained may also be attributed to the change in the geometry of the complex. For square planar complexes with bidentate ligands,  $\Delta \log K$  amounts to  $-0.6$ . For a regular and distorted octahedral geometry, the values are  $-0.4$  and  $-0.9$  units, respectively [6].

(b) The  $\log X$  values in the title systems are in general found to be in the range of the statistically expected values (0.6). The statistically expected  $\log X'$  value is 0.3. In Cu(II) ternary complexes,  $\log X'$  is found to be greater than 0.3, suggesting that *MA* and *MB* bonds in ternary systems are stronger than those in corresponding binary systems. By varying the amino acid in ternary chelates, not big variation is observed in  $\log X'$ . This means that the stabilization of *MA* in ternary systems is influenced by changes in the size of the amino acid. Hence,  $\log X$  values are probably influenced by steric differences of the ligands. The data reveal that  $\log X'$  values of Cd(II) chelates (0.08–0.21) are smaller in magnitude than the statistical value, indicating a marked instability of Cd(II) ternary chelates compared to other species. Thus, it may be concluded that  $\log X$  values are probably influenced by the large size of the Cd(II) ion.

(c) The stability of the investigated ternary complexes can also be calculated using a statistical method [6, 25] according to Eq. (16):

$$\log \beta_{\text{stat}} = \log 2 + 1/2 \cdot \log \beta_{MA_2}^M + 1/2 \cdot \log \beta_{MB_2}^M \quad (16)$$

$\log \beta_{\text{stat}}$  and the difference between stability constants measured and calculated ( $\log \beta_{MAB} - \log \beta_{\text{stat}}$ ) are reported in Table 2. The results indicate that the above difference has a small positive value, reflecting that the *MAB* system is more stable than both *MA<sub>2</sub>* and *MB<sub>2</sub>*. This stability enhancement is referred to as a “ligand effect” which is related to the electrostatic factors originating from charge neutralization: in the formation of *MAB<sup>+</sup>*, one positive charge of *MB<sup>2+</sup>* is neutralized by ligand *B<sup>-</sup>*. This leads to an increase in covalence. Moreover, the enhanced stability can also be explained in terms of metal-to-ligand  $d_{\Pi}$ - $p_{\Pi}$  back bonding which causes the metal ion to be more positive or more electronegative



[38] compared to the hydrated metal ions. This permits stronger  $M \leftrightarrow B$  interaction.

### Distribution diagrams

The percentage of concentration of each complex species as a function of  $pH$  value has been calculated [39]. The  $pH$  distribution profiles for the Cd-Gly binary and Cd-Gly ternary systems, taken as representatives are shown in Figs. 5 and 6, respectively. Similar trends were obtained for the other systems. The distribution profiles for binary systems show that at lower  $pH$  values (2.0–3.0) almost all Cd(II) ions will be present as free ions (88%). In the  $pH$  range of 6.0–7.8, the predominant change is the conversion of Cd(II) into Cd-Gly with a maximum degree of formation (60%) at  $pH = 7.25$ . At a  $pH$  of ca. 9.0, the Cd(II) ions have completely disappeared ( $X = 3.09\%$ ), and Cd-Gly is present to an extent of 8.6% whereas the concentration of Cd(Gly)<sub>2</sub> predominates (78%).

In the case of ternary systems, the plots (Fig. 6) show that between  $pH$  7.5 and 9.3 the concentration of Cd-Gly decreases, whereas the concentration of Cd-Gly-B increases. At  $pH = 8.9$  the ternary system reaches its maximum (57%); the concentrations of binary systems are small.

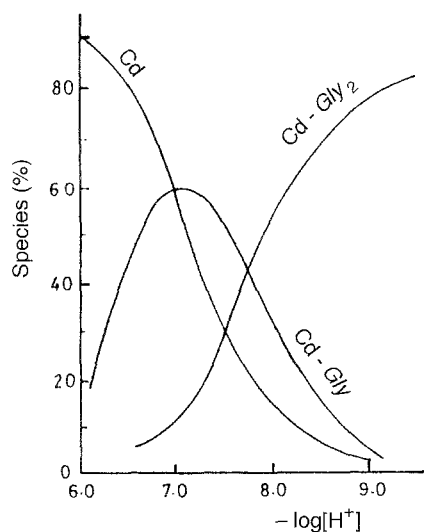


Fig. 5. Species distribution diagrams for Cd(II)-Gly

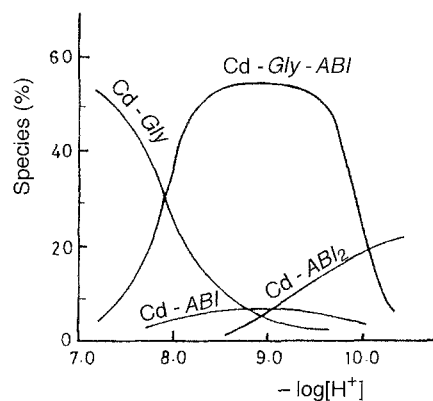


Fig. 6. Species distribution diagrams for Cd(II)-Gly-ABI

### Structure of the complexes

The electronic spectra of the solid complexes in *DMF* solutions show a weak band in the region of 480–520 nm which can be assigned to the  $2E_{2g} - {}^2T_{2g}d \rightarrow d$  transition in a tetragonal distorted octahedral geometry around Cu(II) [40]. The two broad bands located at *ca.* 410 and 430 nm are characterized by high molar absorptivity. Therefore, these bands may be due to an *L-M*(CT) transition [41]. The bonding centers can be deduced on from IR and  ${}^1\text{H}$  NMR evidence:

(i) The IR spectra of the azo ligands *ABA* and *ABI* exhibit a broad band at *ca.*  $3400\text{ cm}^{-1}$  due to the  $\delta(\text{OH})$  mode, and a weak multiplet band in the region of  $3180\text{--}3050\text{ cm}^{-1}$  assigned to  $\delta(\text{NH})$  reflects strong intramolecular H-bonding to the C=O group of the barbiturate ring. The absence of (OH) in the IR spectra of the complexes suggest that the *o*-OH group is involved in bonding.

(ii) In *ABA*, the two strong bands at  $1720$  and  $1660\text{ cm}^{-1}$  are due to free and H-bonded  $\nu(\text{C}=\text{O})$  stretch vibrations, respectively. The absence of the first  $\nu(\text{C}=\text{O})$  complexation indicates Cu–O interaction. The shifts of  $\nu(\text{C}=\text{O})$  stretching located at *ca.*  $1250\text{ cm}^{-1}$  in the free ligand to the carbonyl group in chelation.

(iii) The IR spectra of *ABI* exhibit a band at  $1610\text{ cm}^{-1}$  which can be ascribed to  $\nu(\text{C}=\text{N})$  of the imidazole ring. This band is shifted to lower frequencies on complexation, suggesting that N-3 of the imidazole ring is involved in bonding.

(iv) The strong band appearing in the IR spectra of the free ligands *ABA* and *ABI* at  $1445$  and  $1440\text{ cm}^{-1}$ , respectively, is attributed to the  $\nu(\text{N}=\text{N})$  stretching mode [41]. Upon complexation, this band is shifted to lower frequencies ( $1430\text{--}1415\text{ cm}^{-1}$ ) which confirms the coordination of the nitrogen atom of the azo group to Cu(II). Comparison of the  ${}^1\text{H}$  NMR spectroscopic data of the free ligands with those of their Cu(II) complexes shows that the phenolic *o*-OH proton of the ligands centered at *ca.* 9.2 (*ABA*) and 8.9 (*ABI*) ppm has disappeared, indicating that the hydroxy group is involved in complex formation.

(v) the  ${}^1\text{H}$  NMR spectra of *ABA* show a doublet at 11.1 and 12.3 ppm assigned to the NH protons associated with the barbiturate ring nitrogen atoms N-1 and N-3. The slight broadening of the signals reflects a fast proton exchange with the C=O group [42]. The second NH signal is shifted markedly downfield to *ca.* 13.2 ppm upon complexation, suggesting that the enolic form of *ABA* is involved in chelation.

The combination of the  ${}^1\text{H}$  NMR and IR results reveals that the azo ligands behave as monobasic tridentate chelates through *o*-OH, N=N, and C=O (barbiturate) or N-3 (benzimidazole). This confirms our conclusion that only the phenolic *o*-OH group is deprotonated during complex formation in solution.

## Experimental

### Materials and solutions

All chemicals used were of A. R. grade (Merck) and were used without further purification. 2-(*o*-Hydroxyphenylazo)-2-cyanomethyl benzimidazole (*ABI*) and 5-(*o*-hydroxyphenylazo) barbituric acid (*ABA*) were synthesized according to *Vogel* [16]. The Cu(II) complexes were prepared as described earlier [17]. Ligand stock solutions were prepared by dissolving the calculated amount of substance in 20% (v/v) EtOH-H<sub>2</sub>O and were standardized by titration with standard HClO<sub>4</sub>.

Solutions of the metal ions Cu(II), Zn(II), and Cd(II) (Merck or B. D. H. Products) were prepared in doubly-distilled water. The metal content was determined by complexometric titration with *EDTA* [18]. Carbonate-free solutions of NaOH (0.1 *M*) were prepared and standardized against standard potassium hydrogen phthalate solution. 1.0 *M* NaClO<sub>4</sub> and 0.1 *M* HClO<sub>4</sub> stock solutions were prepared from analytical grade samples immediately prior to use. The solutions were diluted as necessary.

#### *Apparatus and procedures*

The UV/Vis, IR, and <sup>1</sup>H NMR spectra were measured as described before [19]. *pH*-metric titrations were carried out at 37 ± 0.1°C in a double-walled glass cell; pH values were determined with a MV 87 digital pH-meter with an accuracy of ±0.005 units. The following mixtures (total volume: 50 ml) were titrated against CO<sub>2</sub>-free 0.0825 *N* NaOH: HClO<sub>4</sub> (*a*), *a* + amine (*b*), *b* + metal ion (*c*), *a* + azodye (*d*), *d* + metal ion (*e*), and *a* + amine + azo dye + metal ion (*f*). The ionic strength was adjusted to 0.15 *M* by addition of NaClO<sub>4</sub>. Magnetic stirring was performed during all titrations, and oxygen free nitrogen gas was bubbled through the solution before and during titrations. Multiple titrations were carried out for each system. The pH meter readings recorded in 40% (v/v) EtOH-H<sub>2</sub>O were converted to [H<sup>+</sup>] via the relation of *van Uitert* and *Hass* [20].

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