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Potentiometric and spectrometric study: Copper(II), nickel(II) and zinc(II) complexes with potentially tridentate and monodentate ligands

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Abstract. Equilibrium and solution structural study of mixed-metal–mixed-ligand complexes of Cu(II), Ni(II) and Zn(II) with L-cysteine, L-threonine and imidazole are conducted in aqueous solution by potentiometry and spectrophotometry. Stability constants of the binary, ternary and quaternary complexes are determined at 25 ± 1°C and in $I = 0{\cdot}1$ M $NaClO_4$. The results of these two methods are made self-consistent, then rationalized assuming an equilibrium model including the species H_3A, H_2A, A, BH, B, M(OH), $M(OH)_2$, M(A), MA(OH), M(B), M(A)(B), $M_2(A)_2(B)$, $M_2(A)_2(B–H)$, $M^1M^2(A)_2(B)$ and $M^1M^2(A)_2(B–H)$ (where the charges of the species have been ignored for the sake of simplicity) (A = L-cysteine, L-threonine, salicylglycine, salicylvaline and BH = imidazole). Evidence of the deprotonation of BH ligand is available at alkaline *p*H. N_1H deprotonation of the bidentate coordinated imidazole ligand in the binuclear species at $pH > 7{\cdot}0$ is evident from spectral measurements. Stability constants of binary M(A), M(B) and ternary M(A)(B) complexes follow the Irving–Williams order.

Keywords. Homo/hetero-binuclear complexes; imidazole; metal(II); equilibrium study.

1. Introduction

Imidazole as a ligand plays an important role in biological systems, since the imidazole moiety of the histidyl residue in a large number of metalloproteins forms all or part of the binding site of many transition metal ions[1–3]. The imidazolate anion is known to act as a bridging ligand in certain metalloenzymes, for example, in bovine superoxide dismutase[4,5] bridge formation takes place between Cu^{2+} and Zn^{2+} (Cu–B–Zn). Only a few studies have been reported[6,7] on the aqueous coordination chemistry of imidazolate bridged complexes. Recently we reported[8–10] some solution equilibrium studies of imidazolate bridged complexes with Cu^{2+}, Ni^{2+} and Zn^{2+}. The study is now extended by taking potentially tridentate ligands, viz. L-cysteine, L-threonine, salicylglycinate and salicylvalinate, three metal ions (Cu^{2+}, Ni^{2+} and Zn^{2+}) and imidazole. The aqueous coordination chemistry of simple imidazolate bridged metal complexes is explored using *p*H-potentiometric and UV/Vis spectroscopic techniques.

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2. Experimental

2.1 *Materials*

L-Cysteine, L-threonine (s.d. Fine Chem.), imidazole (s.d. Fine Chem.) and copper perchlorate hexahydrate (Aldrich) were used as such. All other chemicals were of AR grade. Standard solution were prepared by using double-distilled CO_2-free water and stored in the refrigerator.

2.2 *pH-metric studies*

*p*H-measurements were made on a Systronics *p*H-meter-235.

The following solutions were prepared in a total volume of 50 ml for *p*H-metric titrations.

(i) $HClO_4$ (0·03 M) + $NaClO_4$ (0·1 M).
(ii) $HClO_4$ (0·03 M) + A (0·003 M) + $NaClO_4$ (0·1 M).
(iii) $HClO_4$ (0·03 M) + B (0·003 M) + $NaClO_4$ (0·1 M).
(iv) $HClO_4$ (0·03 M) + $M(II)(ClO_4)_2$ (0·003 M) + A (0·003 M) + $NaClO_4$ (0·1 M).
(v) $HClO_4$ (0·03 M) + $M(II)(ClO_4)_2$ (0·003 M) + B (0·003 M) + $NaClO_4$ (0·1 M).
(vi) $HClO_4$ (0·03 M) + $M(II)(ClO_4)_2$ (0·003 M) + A (0·003 M) + B (0·003 M) + $NaClO_4$ (0·1 M).
(vii) $HClO_4$ (0·03 M) + $M(II)(ClO_4)_2$ (0·006 M) + A (0·006 M) + B (0·003 M) + $NaClO_4$ (0·1 M).
(viii) $HClO_4$ (0·03 M) + $M^1(II)(ClO_4)_2$ (0·003 M) + $M^2(II)(ClO_4)_2$ (0·003 M) + A (0·006 M) + B (0·003 M) + $NaClO_4$ (0·1 M).

Each of the above samples set was titrated against 1·0 M NaOH. The procedure followed for the *p*H-metric measurements was as described in the literature [11–18]. The formation constants were evaluated using the SCOGS computer programme[19].

2.3 *UV-visible studies*

Aqueous solutions examined by UV-visible spectroscopy were prepared as described above. The optical absorption spectra were recorded on a Systronics UV-visible spectrophotometer-117 with 1 cm quartz cell in aqueous solution at appropriate *p*H values. The extinction coefficients for complexes were also calculated from the solution concentration at the respective absorbance maxima.

3. Results and discussion

3.1 *Proton-ligand formation constants*

Both the aminoacids used are tridentate. The L-cysteine has three coordination sites viz., –COOH, –SH and $–NH_2$, the L-threonine system has –COOH, $–NH_2$, –OH and salgly/salval have –COOH, –OH and >NH groups. The protonation constants for the aminoacids, Sciff bases and imidazole are presented in table 1. These *pK* values correspond to the earlier reported [11–18] values. The overall stability constant values are reported in tables 1–5 and some representative distribution curves are shown in figures 1 and 2.

3.2 *Metal-ligand formation constants of binary (1:1) systems*

The stabilities of different types of species in complexation equilibria depend upon the experimental conditions used. The complexation equilibria of the binary (M^{2+}: A) systems have shown the presence of the following species by stoichiometry: H_3A, H_2A, HA, A, M^{2+}, M(OH), $M(OH)_2$, (MA), MA(OH). Similarly in the M^{2+}:BH(1:1) binary system the species present are BH, B, M(OH), $M(OH)_2$, M(B) and M(B)(OH). Among these binary simple complexes, the stability of hydroxy species have also been considered in calculating the stability constants, since the buffer regions corresponding to metal ligand complex formation equilibria overlap with the hydrolytic equilibria of the M^{2+} (aq.) ions. Ternary hydroxo complexes MA(OH) and M(B)(OH) occur with all the three M^{2+} ions (M = Cu, Ni and Zn); however, the abundance of binary hydroxo species, M(OH) and $M(OH)_2$ is relatively higher with Zn^{2+}. The $\log\beta_{MA}$ and $\log\beta_{MB}$ values obtained in the present work (table 3) correspond to the tridentate and monodentate binding of ligands respectively.

3.3 *Metal-ligand formation constants of ternary (1:1:1/ 2:2:1) systems*

Earlier workers [18,20–25] have studied various types of mononuclear ternary complexes particularly with Zn(II) metal ion under different conditions. Ternary species detected are Zn(A)(BH) and Zn(A)(B) in the Zn(II)-Cys(A)-BH system. The ternary species obtained in the present study differ from the ones reported above. Thus, in the title system with (1:1:1) stoichiometry for M(A)(B) and M(A)(B)(OH), the binary species discussed in §3.2 could also be detected, and the stability constants obtained for the common ternary species are consistent with those obtained by earlier workers [18] (table 4).

Table 1. Stability constants of ligands at 25 ± 1°C and $I = 0{\cdot}1$ M $NaClO_4$ (standard deviations are ± 0·02 in log units).

H^+ complex	L-Cysteine $\log\beta_{00rst}$	L-Threonine $\log\beta_{00rst}$	SalGly $\log\beta_{00rst}$	SalVal $\log\beta_{00rst}$
H_3A	20·82 (19·93)*	–		
H_2A	18·73 (18·53)*	11·51	11·68	11·73
HA	10·36 (10·31)*	9·18	8·24	8·29
BH	7·10	7·10	7·10	7·10

*Ref. 18

Table 2. Hydrolytic constants ($\log\beta_{p000t}$) of M^{2+} ions.

Complex	Ni(II)	Cu(II)	Zn(II)
$M(OH)^+$	– 8·10	– 7·29	– 7·89
$M(OH)_2$	– 16·87	– 13·10	– 14·92

*Ref. 18

Table 3. Stability constants (logβ_{porst}) of M^{2+} complexes (binary complexes) at 25 ± 1°C and I = 0·1 M $NaClO_4$ (standard deviations are ± 0·002 in log units).

	L-Cysteine			L-Threonine			Salicylglycine			Salicylvaline		
Complex	Ni(II)	Cu(II)	Zn(II)	Ni(II)	Cu(II)	Zn(II)	Ni(II)	Cu(II)	Zn(II)	Ni(II)	Cu(II)	Zn(II)
MA	10·87	12·09	9·61	7·25	8·80	6·03	2·80	5·38	3·13	2·91	5·41	3·17
			(9·64)*				(2·84)*	(5·33)*	(3·10)*			
MA(OH)	− 1·50	1·00	− 3·00	− 1·90	0·90	− 3·25	− 2·30	− 0·70	− 2·60	− 1·50	1·00	− 3·10
M(B)	3·65	4·31	2·53	− 3·65	− 4·31	− 2·53	3·65	4·31	2·53	3·65	4·31	2·53
			(2·55)*									

*Ref. 18

Table 4. Stability constants (logβ_{porst}) of M^{2+} ternary complexes at 25 ± 1°C and I = 0·1 M $NaClO_4$ (standard deviations are ± 0·002 in log units).

	L-Cysteine			L-Threonine			Salicylglycine			Salicylvaline		
Complex	Ni(II)	Cu(II)	Zn(II)	Ni(II)	Cu(II)	Zn(II)	Ni(II)	Cu(II)	Zn(II)	Ni(II)	Cu(II)	Zn(II)
MA(B)	13·27	17·33	11·53	10·13	12·61	8·86	5·83	8·53	5·01	6·63	8·90	5·50
			(12·22)*									
M^2A_2(B)	29·37	32·17	28·89	21·81	24·73	18·76	15·14	18·50	14·50	17·58	21·22	16·67
M^2A_2(B–H)	22·31	26·04	21·26	13·83	18·01	12·13	8·60	13·06	6·07	10·67	15·20	9·81
	(7·06)	(6·13)	(7·63)	(7·98)	(6·72)	(6·63)	(6·54)	(5·44)	(8·43)	(6·91)	(6·02)	(6·86)

*pK values of homobinuclear complexes are shown in parentheses

Table 5. Stability constants (logβ_{porst}) of M^{2+} quaternary complexes at 25 ± 1°C and I = 0·1 M $NaClO_4$ (standard deviations are ± 0·002 in log units).

	L-Cysteine			L-Threonine			Salicylglycine			Salicylvaline		
Complex	Cu–Zn	Cu–Ni	Zn–Ni	Cu–Zn	Cu–Ni	Zn–Ni	Cu–Zn	Cu–Ni	Zn–Ni	Cu–Zn	Cu–Ni	Zn–Ni
$M^1M^2A_2$(B)	30·77	31·87	29·67	22·11	24·03	21·73	18·83	12·24	16·53	20·05	12·68	18·38
$M^1M^2A_2$(B–H)	23·89	24·23	22·57	15·23	14·87	13·03	11·86	5·63	9·67	13·75	5·83	12·25
	(7·88)	(7·64)	(7·10)	(6·88)	(9·16)	(8·70)	(6·97)	(6·61)	(6·86)	(6·30)	(6·85)	(6·13)

*pK values of heterobinuclear complexes are shown in parentheses

The M^{2+}: A:BH (2:2:1) system in the *p*H range ~5–6·5 suggests the formation of homo-binuclear $M_2(A)_2(B)$ complexes. The formation of homo-binuclear complexes takes place according to the following equilibrium:

$$2Cu(A) + BH \rightleftharpoons Cu_2(A)_2(B) + H^+.$$

Binuclear complexes with the other two metal ions are, however, found to be formed according to the equilibria:

$$M(II) + HA + BH \rightleftharpoons MA(B) + 2H^+,$$

$$2M(II) + 2HA + BH \rightleftharpoons M_2(A)_2(B) + 3H^+.$$

Figure 1 shows the species distribution curves of homo-binuclear complexes.

3.4 *Quaternary (1:1:2:1) systems*

Species distribution curves for the quaternary systems are presented in figure 2. The titration curves of all present quaternary systems are similar to one another. The titration curves of various quaternary systems show only one equivalent point (*p*H ~ 7·0) which is attributed to the formation of quaternary species according to the following general equation,

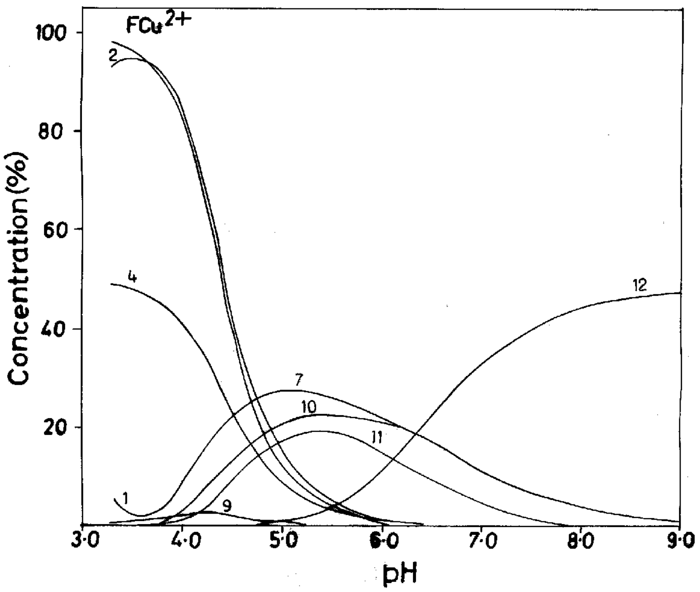


Figure 1. Species distribution curves of 2:2:1, Cu^{2+}: AH:BH (A = L-cysteine) system: (1) H_3A (2) H_2A, (3) HA, (4) BH, (5) Cu(OH), (6) $Cu(OH)_2$, (7) CuA, (8) Cu(A)(OH), (9) Cu(B), (10) Cu(A)(B), (11) $Cu_2(A)_2(B)$ and (12) $Cu_2(A)_2(B–H)$.

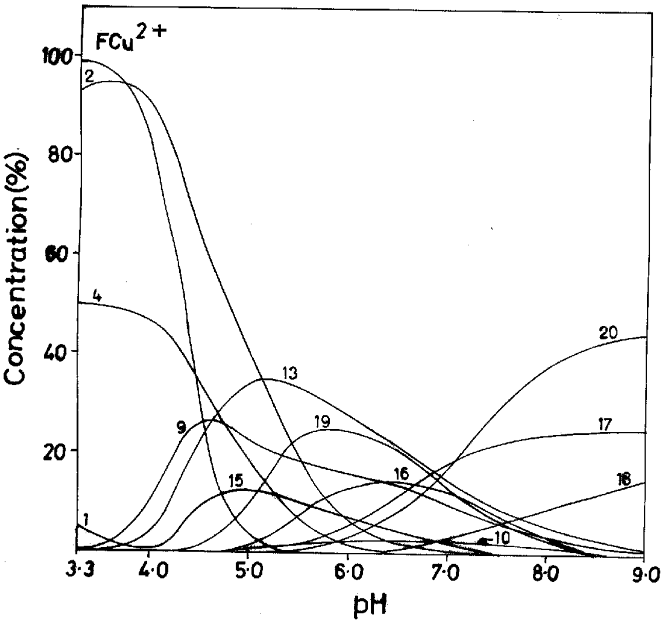
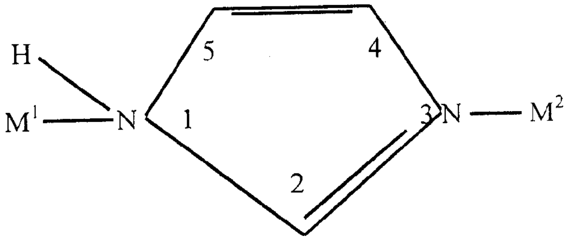


Figure 2. Species distribution curves of 1:1:2:1, Cu^{2+}:Zn^{2+}:AH:BH (A = L-cysteine) system: (1) H_3A, (2) H_2A, (3) HA, (4) BH, (5) Cu(OH), (6) $Cu(OH)_2$, (7) Zn(OH), (8) $Zn(OH)_2$, (9) CuA, (10) Zn(A), (11) Cu(A)(OH), (12) Zn(A)(OH), (13) Cu(A) (B), (14) Zn(A)(B), (15) $Cu_2(A)_2(B)$, (16) $Zn_2(A)_2(B)$, (17) $Cu_2(A)_2(B–H)$, (18) $Zn_2(A)_2(B–H)$, (19) $CuZn(A)_2(B)$ and (20) $CuZn(A)_2(B–H)$.



($M^1 = M^2$ or $M^1 \neq M^2$)

Chart 1.

$$M^1(A) + BH + M^2A \rightleftharpoons M^1M^2(A)_2(B).$$

All ligands used except imidazole provide (S, N, O^-) terdentate chelation to the metal ion M(II) ions in M(A) and M(A)(B) complexes. The imidazole in the ternary (1:1:1) complexes functions as monodentate ligand coordinating through pyridine nitrogen [26]. Simultaneous occurance of mononuclear ternary complexes M(A)(B) and homo/hetero-binuclear ternary complex systems suggest (N_1, N_3) bridging bidentate coordination by the imidazole ligand in binuclear complexes (chart 1).

3.5 *Deprotonated systems*

The quaternary titration curves show the second buffer zone at *p*H ~8·0 which is attributed to the formation of a deprotonated species. The possible site for deprotonation may be the N_1H of the bridging ligand according to the following general equilibrium,

$$M_2(A)_2(B) \rightleftharpoons M_2(A)_2(B\text{–}H) + H^+.$$

The deprotonation constants were also evaluated and are presented in tables 4 and 5. These deprotonation constants of bridging bidentate coordinated imidazole are found to be lower for Cu^{2+} and Ni^{2+} ions presumbly because of stronger $M(d\pi) \rightarrow B(\pi)$ interaction, due to which the electron density on the imidazole ligand is increased, and this disfavours the release of the N_1H proton. Such π-bonding is, of course, absent in the corresponding Zn^{2+} complexes. Consequently, coordinated imidazole in the homo-binuclear Zn^{2+} complex $(Zn)_2(A)_2B$ shows higher acidity relative to complexes with Ni^{2+}

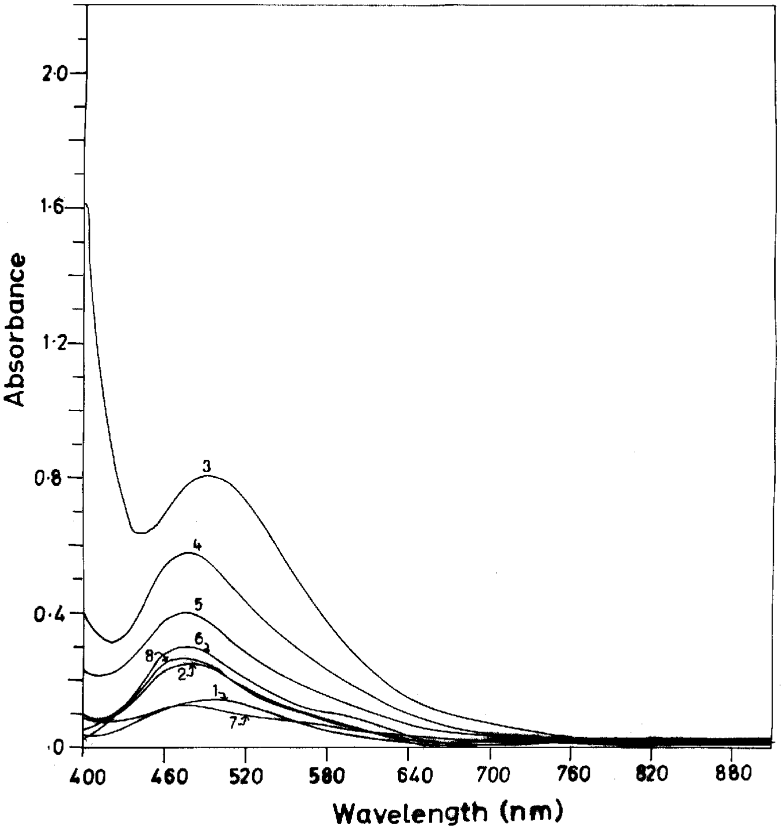


Figure 3. Visible spectra for different complexes containing Ni^{II}, (1) Ni(A), *p*H 6·0, (2) Ni(A)(B), *p*H 7·0, (3) $Ni_2(A)_2(B)$, *p*H 6·5, (4) $Ni_2(A)_2(B\text{–}H)$, *p*H 8·5, (5) CuNi $(A)_2(B)$, *p*H 6·5, (6) $CuNi(A)_2(B\text{–}H)$, *p*H 8·5, (7) $NiZn(A)_2(B)$, *p*H 6·5 and (8) $NiZn(A)_2(B\text{–}H)$, *p*H 8·5.

and Cu^{2+}. The imidazole anion, $(B–H)^{-}$, may provide (N_1, N_3) bridging bidentate coordination in the $M_2(A)_2(B–H)$ and $M^1M^2(B–H)$ complex, exactly in the same manner that the active site of the imidazole residue of histidine-61 at the active site of bovine superoxide dismutase coordinates one Cu^{2+} ion and one Zn^{2+} ion [27].

3.6 *Formation constants with respect to metal ion*

Stability constants of the binary M(A), M(B) and ternary M(A)(B) complex follow the Irving–Williams order [28,29]. In general, stability constants of the binuclear complexes are in the order: CuCu > CuNi > CuZn > ZnNi > NiNi > ZnZn. Slightly higher stability of the NiZn hetero-binuclear complex over the corresponding NiNi and ZnZn complexes is observed. The single $Ni(d\pi) \rightarrow B(\pi)$ back-bonding in the $NiZn(A)_2(B)$ complex adds to its stability, whereas two opposing $Ni(d\pi) \rightarrow B(\pi)$ bonds in the $Ni_2(A)_2(B)$ complex possibly mutually weaken each other. As a result, the stability of the Ni–Ni complex is slightly lower than that of the Ni–Zn complex.

3.7 *Absorption spectra*

The *p*H-dependence visible absorption spectra are recorded for different nickel(II) binary, ternary and quaternary systems with L-cysteine. The spectra are shown in figure 3 and visible absorption data are presented in tables 6 and 7. The nickel(II)–L-cysteine (1:1) complex shows λ_{max} at 492 nm whereas the nickel(II)–L-cysteine–B (1:1:1) systems shows λ_{max} at 476 nm. This decrease in λ_{max} is due to the fourth ligand (imidazole). This

Table 6. Spectrophotometirc data for nickel(II) complexes with L-cysteine, L-threonine and imidazole.

Composition	Complex	*p*H	λ_{max} (nm)	ε ($dm^3\,mol^{-1}\,cm^{-1}$)
(A) Complexes with L-cysteine				
Ni^{2+}: AH (1:1)	Ni(A)	6·0	492	47
Ni^{2+}: AH:BH (1:1:1)	Ni(A)(B)	7·0	476	84
Ni^{2+}: AH:BH (2:2:1)	$Ni_2(A)_2(B)$	6·5	496	179
NI^{2+}: AH:BH (2:2:1)	$Ni_2(A)_2(B–H)$	8·5	480	191
Cu^{2+}: Ni^{2+}:AH:BH (1:1:2:1)	$CuNi(A)_2(B)$	6·5	476	40
Cu^{2+}: Ni^{2+}:AH:BH (1:1:2:1)	$CuNi(A)_2(B–H)$	8·5	476	86
Ni^{2+}: Zn^{2+}:AH:BH (1:1:2:1)	$NiZn(A)_2(B)$	6·5	478	133
Ni^{2+}: Zn^{2+}:AH:BH (1:1:2:1)	$NiZn(A)_2(B–H)$	8·5	476	99
(B) Complexes with L-threonine				
Cu^{2+}: AH (1:1)	Cu(A)	6·0	735	16
Cu^{2+}: AH:BH (1:1:1)	Cu(A)(B)	7·0	684	36
Cu^{2+}: AH:BH (2:2:1)	$Cu_2(A)_2(B)$	6·5	695	60
Cu^{2+}: AH:BH (2:2:1)	$Cu_2(A)_2(B–H)$	8·5	642	93
Cu^{2+}: Zn^{2+}:AH:BH (1:1:2:1)	$CuZn(A)_2(B)$	6·5	637	50
Cu^{2+}: Zn^{2+}:AH:BH (1:1:2:1)	$CuZn(A)_2(B–H)$	8·5	640	76
Cu^{2+}: Ni^{2+}:AH:BH (1:1:2:1)	$CuNi(A)_2(B)$	6·5	644	50
Cu^{2+}: Ni^{2+}:AH:BH (1:1:2:1)	$CuNi(A)_2(B–H)$	8·5	637	59

Table 7. Spectrometric data for copper(II) complexes with salicylglycine, salicylvaline and imidazole.

			Salicylglycine		Salicylvaline	
Composition	Complex	*p*H	λ_{max} (nm)	ε (dm^3 mol^{-1} cm^{-1})	λ_{max} (nm)	ε (dm^3 mol^{-1} cm^{-1})
Cu^{2+}: AH (1:1)	Cu(A)	6.5	626	37	623	72
Cu^{2+}: AH:BH (1:1:1)	Cu(A)(B)	7.0	638	66	627	87
Cu^{2+}: AH:BH (2:2:1)	$Cu_2(A)_2(B)$	7.5	630	78	648	143
Cu^{2+}: AH:BH (2:2:1)	$Cu_2(A)_2$(B-H)	8.5	630	74	637	158
Cu^{2+}: Zn^{2+}:AH:BH (1:1:2:1)	$CuZn(A)_2(B)$	7.5	627	56	634	66
Cu^{2+}: Zn^{2+}:AH:BH (1:1:2:1)	$CuZn(A)_2$(B-H)	8.5	627	55	616	75
Cu^{2+}: Ni^{2+}:AH:BH (1:1:2:1)	$CuNi(A)_2(B)$	7.5	619	30	620	90
Cu^{2+}: Ni^{2+}:AH:BH (1:1:2:1)	$CuNi(A)_2$(B-H)	8.5	619	30	620	106

ligand exerts higher ligand fields than L-cysteine and also is attached in the equatorial position of nickel(II). As is known, however, the axial coordination in metal(II) complexes results in a blue shift of the electron absorption spectra[30]. The nickel(II) binuclear complex formed at *p*H 6·5 shows λ_{max} at 496 nm. The λ_{max} of this binuclear species is greater than that of mononuclear ternary complexes. The enhanced λ_{max} value due to the average ligand field exerted by the bridging imidazole ligand (BH) on the nickel(II) ion in $Ni_2(A)_2(B)$ is definitely weaker than the field exerted by the same ligand (BH) when it is coordinates a single nickel(II) ion as monodentate ligand in the mononuclear ternary complex, Ni(A)(B). On raising the *p*H to 8·5 the observed λ_{max} value is 480 nm. This decrease in λ_{max} is due to the N_1H deprotonation of the bridging imidazole ligand (BH) in the binuclear species $Ni_2(A)_2$(B–H), that provides an additional electron to the bridging ligand (BH). The resulting (B–H) anion in the deprotonated complex, $Ni_2(A)_2$(B–H), obviously exerts a stronger ligand field than that exerted by the neutral ligand (BH). As a consequence, this deprotonated complex absorbs at slightly shorter wavelength. This is clearly evident from the blue shifts in absorption maxima by ~15 nm on increasing the *p*H of the same binuclear system. Therefore our results suggest metal promoted deprotonation and also that coordination of the fourth ligand in the simple ternary nickel(II) system is at the equatorial position of the Ni(A)B species. We have also recorded the *p*H-dependence visible absorption spectra for different copper(II) binary, ternary and quaternary systems using L-threonine salGly and salVal. Visible absorption data are presented in tables 6 and 7. The copper(II)–L-threonine (1:1) complex yields λ_{max} at 735 nm whereas the copper(II)–L-threonine–imH (1:1:1) system yields λ_{max} at 684 nm. This decrease in λ_{max} is due to the fourth ligand (imidazole). The copper(II) binuclear complex formed as *p*H 6·5 shows λ_{max} at 695 nm. The λ_{max} of this binuclear species is greater than that of the mononuclear ternary complexes. On further raising the *p*H to 8·5 the obtained λ_{max} value is 642 nm. This decrease in λ_{max} is due to the N_1H deprotonatin of the bridging imidazole ligand (imH) in the binuclear species $Cu_2(A)_2$(B–H) that provides an additional electron to the bridging ligand (B–H).

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