

Studies on Some Sulphonamidobenzimidazoles as Metal Complexing Ligands: Part II—Study of the Complex Formation of 2-(1'-Benzenesulphonylamino-3'-methylmercapto)propylbenzimidazole with Cobalt(II), Nickel(II), Copper(II) & Zinc(II)

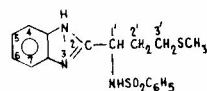
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Received 27 June 1983; revised and accepted 29 December 1983

Study of the complex formation equilibrium in the reactions of Co(II), Ni(II) and Zn(II) with the newly synthesized ligand, 2-(1'-benzenesulphonylamino-3'-methylmercapto)propylbenzimidazole (BMPBzH or LH) in 50% (v/v) water-dioxan medium at a constant ionic strength $\mu = 0.2 M$ (NaNO₃) indicates the formation of complexes of the types ML^+ , ML_2 in the pH range 6.5-9.0 and of $M(H_{-1}L)(L)^-$ and $M(H_{-1}L)_2^-$ at pH > 9.5. Complexation of the ligand with Cu(II) occurs at much lower pH values and CuL₂ precipitates at pH $\approx$ 4.5. Proton-ligand and metal-ligand stability constants have been determined at 20, 30 and 40°C and the thermodynamic parameters associated with the complexation equilibria have been evaluated. Stabilities of the complexes have been correlated with the nature of the metal ions, denticity of the ligand and nature of metal-ligand bonds.

We have recently synthesised a new sulphonamido-benzimidazole ligand, 2-(1'-benzenesulphonylamino-3'-methylmercapto)propylbenzimidazole¹ (BMPBzH or LH, structure I) which showed antibacterial activity² against several bacteria. The activity was found to be enhanced profoundly in the presence of Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ ions. Studies on the complex formation equilibria of these metal ions with the biologically active ligands such as BMPBzH are essential for understanding the mechanism of their antibacterial actions. The present paper describes a pH metric study of the complex formation of Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ with the ligand BMPBzH in 50% (v/v) water-dioxan medium at a constant ionic strength, $\mu = 0.2 M$ (NaNO₃) at three temperatures, 20, 30° and 40°C, following Bjerrum's method³ as applied by Irving and Rossotti⁴.



Structure I (BMPBzH)

Materials and Methods

The ligand BMPBz was synthesised by condensing *o*-phenylenediamine (3.24 g, 0.03 mol) with *N*-benzenesulphonyl methionine⁵ (8.7 g, 0.03 mol) by the fusion method⁶ at 155°C. The resultant blue sticky mass was cooled to room temperature, extracted with acetone, norited, filtered and diluted with equal volume of water and the pH of the mixture was adjusted to $\approx$ 8, by adding aqueous ammonia solution. BMPBzH separated as a white crystalline solid. It was

further purified by recrystallization from aqueous ethanol. The resultant needle shaped crystals were dried *in vacuo*, m.p., 182-183°C. It gave satisfactory C and H analyses for the composition C₁₇H₁₉N₃O₂S₂. All the other reagents were either of AR quality or were properly purified. Their solutions were prepared in doubly distilled CO₂ free water and purified dioxan⁷. Concentrations of metal ions and associated free nitric acid in the metal nitrate solutions were determined by ion exchange separation coupled with combined acid-base and complexometric titrations⁸. Carbonate free sodium hydroxide solution was prepared⁹ from AR sodium hydroxide pellets.

pH measurements were made with a Systronics digital pH meter model 335 (accuracy ± 0.01 pH units) using a glass electrode of pH range 1-13 in conjunction with a saturated calomel electrode. The pH meter was calibrated using aqueous buffer solutions of pH 4, 7 and 9. For the determination of the proton-ligand and metal-ligand formation constants the following solutions were prepared:

- 0.01 *M* HNO₃
- 0.01 *M* HNO₃ + 0.01 *M* ligand BMPBzH in the form of BMPBzH₂⁺
- 0.01 *M* HNO₃ + 0.001-0.002 *M* metal nitrate
- 0.01 *M* HNO₃ + 0.01 *M* ligand BMPBzH in the form of BMPBzH₂⁺ + 0.001-0.002 *M* metal nitrate
- 0.01 *M* HNO₃ + 0.01 *M* 2-methylbenzimidazole (Bz) in the form of BzH⁺

Each solution was prepared in 25 ml (50% v/v) water-dioxan and titrated against 0.125 *M* NaOH in the same solvent medium maintaining a constant ionic strength

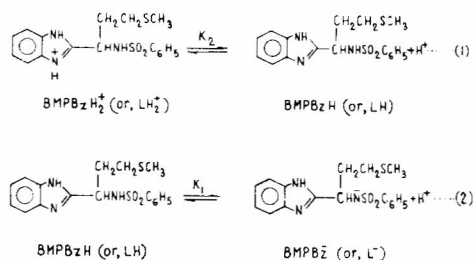
($\mu = 0.2 M$) by adding requisite amounts of NaNO_3 , at three different temperatures 20° , 30° and 40°C .

Hydrogen ion concentrations $[\text{H}^+]$ at different $p\text{H}$ meter readings were obtained as usual^{10,11} from a plot of $-\log [\text{H}^+]$ or $-\log [\text{OH}^-]$ against the $p\text{H}$ meter reading using the titration data of the solution (i) and the ionic product of water at the respective temperature¹². Various concentration variables, viz. $\bar{n}_\text{H}$, $\bar{n}_{\text{LH}}$, $\bar{n}_\text{L}$, $\bar{n}_\text{h}$, $[\text{LH}]$, $[\text{L}]$ etc. required for the evaluation of proton-ligand and metal-ligand formation constants were calculated⁴ from the $p\text{H}$ titration curves. Representative titration curves for complexation of the ligand with Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} at 30°C are shown in Fig. 1.

Results and Discussion

Proton-ligand constants (K_2 and K_1)

$p\text{H}$ -metric titration curve of solution (ii) (curve 2, Fig. 1) containing the ligand BMPBzH in the form of BMPBzH_2^+ (or LH_2^+) and a known amount of free nitric acid showed two buffer regions, one in the $p\text{H}$ range 2.5-5.0 and the other in the $p\text{H}$ range 9.5-12.0. In each of these two buffer regions one mol of base per mol of the ligand BMPBzH was consumed. The lower $p\text{H}$ buffer region is undoubtedly due to the deprotonation of benzimidazolium ion as shown in Scheme 1. The higher $p\text{H}$ buffer region is due to the deprotonation of the sulphonamide group, $-\text{SO}_2\text{NH}-$ and not due to the loss of proton from the $-\text{NH}-$ of the benzimidazole ring, as 2-methylbenzimidazolium ion, BzH_2^+ , titrated as a monoprotic acid in the whole $p\text{H}$ range 2.5-12.0 (curve 5, Fig. 1). Deprotonation equilibria of BMPBzH_2^+ (LH_2^+) may, therefore, be represented as follows:



Scheme 1: Deprotonation of the ligand BMPBzH_2^+ (or, LH_2^+) ion

The stepwise stoichiometric deprotonation constants K_2 and K_1 were evaluated¹³ by analysing the $\bar{n}_\text{H}$ (average number of protons bound to the ligand L^- ion) and $p[\text{H}]$ data in the lower and higher $p\text{H}$ buffer regions respectively of the titration of solution (ii). Refined values pK_2 and pK_1 together with the ΔG , ΔH and ΔS values at 30°C are given in Table 1.

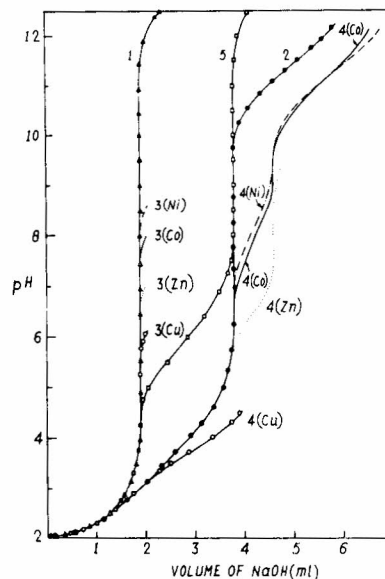
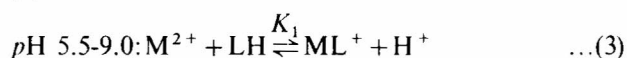


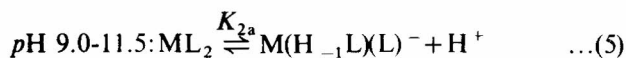
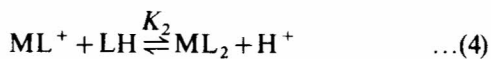
Fig. 1— $p\text{H}$ titration curves at $30 \pm 1^\circ\text{C}$. $\mu = 0.2 M$ (NaNO_3) in 50% (v/v) water-dioxan [Curve 1: $0.01 M \text{HNO}_3$ ($\Delta-\Delta$); Curve 2: $0.01 M \text{HNO}_3 + 0.01 M \text{BMPBzH}$ in the form BMPBzH_2^+ ($\bullet-\bullet$); Curves 3: $0.01 M \text{HNO}_3 + 0.002 M \text{M}(\text{NO}_3)_2$, where $\text{M} = \text{Co}, \text{Ni}, \text{Cu}$ and Zn given in the parentheses $3(\text{Co})$, ($-$); $3(\text{Ni})$, ($-\cdot-\cdot$); $3(\text{Cu})$, ($\circ-\circ$); $3(\text{Zn})$, ($-----$); curves 4: $0.01 M \text{HNO}_3 + 0.01 M \text{BMPBzH}_2^+ + 0.002 M \text{M}(\text{NO}_3)_2$ as in curves 3; $4(\text{Co})$, ($-$); $4(\text{Ni})$, ($-\cdot-\cdot$); $4(\text{Cu})$, ($\circ-\circ$); $4(\text{Zn})$, ($-----$); curve 5: $0.01 M \text{HNO}_3 + 0.01 M$ 2-methylbenzimidazole (Bz) in the form of BzH^+ ($\square-\square$)

Complex formation of Co(II) , Ni(II) and Zn(II) with the ligand BMPBzH

$p\text{H}$ -metric titration of solution (iv) of BMPBzH_2^+ in the presence of M^{2+} ions ($\text{M} = \text{Co}, \text{Ni}$ and Zn) exhibited two buffer regions, one in the $p\text{H}$ range 5.5-9.0, where two mol of base per mol of metal were consumed, and the other in the $p\text{H}$ range 9.0-11.5, where more than one mol of base per mol of metal ion was consumed (curve 4, Fig. 1).

Infrared spectral study¹ of the 1:2 (metal:ligand) complexes, viz. $\text{Co}(\text{BMPBz})_2$ and $\text{Ni}(\text{BMPBz})_2$, which were isolated at $p\text{H} \approx 8$, showed the presence of deprotonated sulphonamido groups¹⁴ in these complexes. As the ligand existed almost exclusively in the neutral BMPBzH (or LH) form in the $p\text{H}$ range 5.5-9.0, complex formation of the ligand with M^{2+} ($\text{Co}, \text{Ni}, \text{Zn}$) ions in this $p\text{H}$ range with the liberation of two protons per metal ion, therefore, involved metal assisted deprotonation of the sulphonamido group of the ligand BMPBzH in a stepwise manner as shown by Eqs (3) and (4). The subsequent release of two protons per metal ion in the higher $p\text{H}$ region (9.0-11.5), therefore, involved deprotonation of $-\text{N}_1\text{H}-$ group of the imidazole ring as a consequence of $\text{N}(\text{imidazole}) \rightarrow \text{M}$ sigma bond formation according to Eqs (5) and (6):





where $H_{-1}L^{2-}$ stands for the ligand species in which the ligand, ion $BMPBz^-$ (or L^-), has lost one proton from the imidazole ring. Examination of free metal ion titration curves (curve 3, Fig. 1) of solutions (iii) showed that hydroxo complex formation had negligible effect on the formation of complexes ML^+ and ML_2 . The stepwise stoichiometric formation constants K_1 and K_2 of the complexes ML^+ and ML_2 and the successive deprotonation constants K_{2a} and K_{1a} of the complexes ML_2 were evaluated by graphical solution of the formation functions (7) and (8) respectively:

$$\bar{n} = (K_1[L^-] + 2K_1K_2[L^-]^2) / (1 + K_1[L^-] + K_1K_2[L^-]^2) \quad \dots(7)$$

$$\bar{n}_h = (2 + K_{2a}/[H^+]) / (1 + K_{2a}[H^+] + K_{2a}K_{1a}/[H^+]^2) \quad \dots(8)$$

where $\bar{n}$ = average number of ligand, L^- , ions bound per metal ion; $[L^-]$ = equilibrium concentration of L^- ion; $\bar{n}_h$ = average number of protons bound to the complex, ML_2 ; $[H^+]$ = equilibrium concentration of hydrogen ion.

The values of $\bar{n}$, $[L^-]$ and $\bar{n}_h$ for the reactions (3)-(6) were calculated using the following mass balance equations for hydrogen ion, ligand and metal, which hold good in different solutions at equilibrium, viz., For solution (i):

$$[H^+] = A' + [OH^-] - B' \quad \dots(9)$$

For solution (ii):

$$T_L'' = [LH_2]'' + [LH]'' + [L^-]'' \quad \dots(10)$$

$$[H^+]'' = A'' + [OH^-]'' - B'' + [LH]'' + 2[L^-]'' \quad \dots(11)$$

and for solution (iv):

$$T_M''' = [M^{2+}]''' + [ML^+]''' + [ML_2]''' + [M(H_{-1}L)(L)^-]''' + [M(H_{-1}L)_2^{2-}]''' \quad \dots(12)$$

$$T_L''' = [LH_2]''' + [LH]''' + [L^-]''' + [ML^+]''' + 2\{[ML_2]''' + [M(H_{-1}L)(L)^-]''' + [M(H_{-1}L)_2^{2-}]'''\} \quad \dots(13)$$

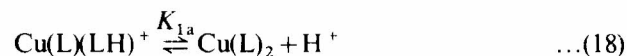
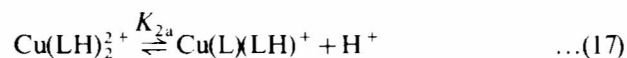
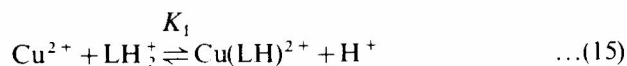
$$[H^+]''' = A''' + [OH^-]''' - B''' + T_L''' + [L^-]''' + [ML^+]''' + 2[ML_2]''' + 3[M(H_{-1}L)(L)^-]''' + 4[M(H_{-1}L)_2^{2-}]''' \quad \dots(14)$$

Here A , B , T_L and T_M primes stand for the final concentrations of free nitric acid, sodium hydroxide, the ligand in the form of LH_2^+ and M^{2+} ion respectively in different solutions at equilibrium. The terms within the brackets, $[]$, represent the

equilibrium concentrations of the respective species. $\bar{n}$, $p[L]$ and $\bar{n}_h$ values were calculated following the procedure of Irving and Rossotti⁴. Refined values¹¹ of the constants K_1 , K_2 , K_{2a} and K_{1a} at three different temperatures 20°, 30° and 40°C and the thermodynamic parameters¹⁵ corresponding to data at 30°C are given in Table 1.

Complex formation of copper(II) with $BMPBzH$

Solution (iv) of the ligand, $BMPBzH_2^+$ ion, containing copper(II) exhibited a flat buffer region in the pH range 2.5-4.5 [curve 4(Cu), Fig. 1], below the buffer region for the deprotonation equilibrium (1) of the ligand LH_2^+ ion. Deprotonation (1) of LH_2^+ was, therefore, facilitated in the presence of Cu(II). At pH 4.5-5.0, a blue compound separated from the solution. Elemental analyses of this compound corresponded to the formula $Cu(BMPBz)_2 \cdot 2H_2O$ or $Cu(L)_2 \cdot 2H_2O$ and its IR spectrum showed the presence of deprotonated sulphonamido groups N-bonded to the metal¹⁴. Complexation of copper(II) with the ligand was, therefore, assumed to take place as follows:



The relevant concentration variables, viz. $\bar{n}_{LH}$ (average number of ligands, LH, bound to Cu(II) ion), $[LH]$, $\bar{n}_h$ (average number of dissociable protons in the complex $Cu(LH)_2^{2+}$ ion) were calculated using the following mass balance equations (Eqs 19-21), in addition to Eqs 9-11, assuming the concentration of L^- ion to be negligible at pH 2.5-4.5.

$$T_{Cu}''' = [Cu^{2+}]''' + [Cu(LH)^{2+}]''' + [Cu(LH)_2^{2+}]''' + [Cu(L)(LH)^+]''' + [Cu(L)_2]''' \quad \dots(19)$$

$$T_L''' = [LH_2]''' + [LH]''' + [Cu(LH)^{2+}]''' + 2\{[Cu(LH)_2^{2+}]''' + [Cu(L)(LH)^+]''' + [Cu(L)_2]'''\} \quad \dots(20)$$

$$[H^+]''' = A''' + [OH^-]''' - B''' + [LH]''' + [Cu(LH)^{2+}]''' + 2[Cu(LH)_2^{2+}]''' + 3[Cu(L)(LH)^+]''' + 4[Cu(L)_2]''' \quad \dots(21)$$

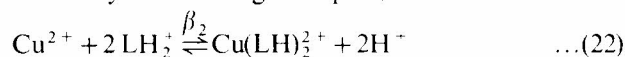
To avoid overlapping of equilibria (15) and (16) with the equilibria (17) and (18), the $\bar{n}_{LH}$ and $[LH]$ values were calculated using the data at the early stages of titration of solution (iv) for copper assuming the concentration of the complexes $Cu(L)(LH)^+$ and

Table 1—Proton-Ligand and Metal-Ligand Stability Constants of Complexes with BMPBzH

[Solvent: Dioxan-Water (50% v/v), $\mu=0.2 M$ (NaNO₃); Temp.: 20 ± 1 , 30 ± 1 and $40 \pm 1^\circ C$]

Proton/ metal ion	Parameter	Temperature, $^\circ C$			Thermodynamic functions at $30 \pm 1^\circ C$		
		20 ± 1	30 ± 1	40 ± 1	ΔG (kcal mol^{-1})	ΔH (kcal mol^{-1})	ΔS (e.u.)
H	pK_2	4.02	3.92	3.88	5.4	-2.9	8
	pK_1	10.30	10.05	9.82	14.0	-9.5	15
Co(II)	$\log K_1$	5.08	5.10	5.12	7.1	+0.5	22
	$\log K_2$	6.12	6.05	6.00	8.4	-2.5	36
	pK_{2a}	9.32	9.03	8.78	12.5	-12.1	1
	pK_{1a}	9.83	9.45	9.13	13.1	-14.3	-4
Ni(II)	$\log K_1$	5.06	5.23	5.40	7.3	7.6	49
	$\log K_2$	4.50	4.67	4.82	6.5	7.2	45
	pK_{2a}	9.20	9.03	8.82	12.5	-13.0	-2
	pK_{1a}	9.80	9.55	9.30	13.2	-12.5	+3
Zn(II)	$\log K_1$	6.11	6.27	6.41	8.7	6.5	30
	$\log K_2$	5.72	5.90	6.12	8.2	7.9	53
	pK_{2a}	8.46	8.22	7.98	11.4	-12.7	-4
	pK_{1a}	9.09	8.80	8.48	12.2	-12.7	-2
Cu(II)	$\log \beta_2$	5.08	4.96	4.86	7.0	-5.1	6
	pK_{2a}	4.19	4.11	4.04	5.7	-3.3	8
	pK_{1a}	4.66	4.59	4.56	6.4	-2.1	14

$Cu(L)_2$ to be negligible in comparison to those of the other species. Also, the $\bar{n}_h$ values were calculated using the data at the later stages of the titration assuming the concentrations of the free Cu^{2+} ion and the complex $Cu(LH)_2^{2+}$ to be negligible. The formation curve ($\bar{n}_{LH}$ versus pLH plot) showed a steep rise in the middle portion. The linear plot of $\{(2 - \bar{n}_{LH})[LH]/(\bar{n}_{LH} - 1)\}$ versus $\{\bar{n}_{LH}/(\bar{n}_{LH} - 1)[LH]\}$ passes through the origin thereby indicating the significance of the term K_1K_2 (i.e. β_2 , the overall formation constant of the complex $Cu(LH)_2^{2+}$ ion) only, and the non-existence of the stepwise constants K_1 and K_2 independently. Two ligands (LH), therefore, bind copper(II) simultaneously¹¹ according to Eq. 22,



rather than in stepwise manner as shown by Eqs (15) and (16). The deprotonation constants K_{2a} and K_{1a} were evaluated by analysing the $\bar{n}_h$, $p[H]$ data graphically. Refined values of $\log \beta_2$ were obtained from a graphical solution of the function

$$\bar{n}_{LH} = 2[LH]^2 / (1 + b\beta_2[LH]^2) \quad \dots(23)$$

$$\text{where } b = 1 + K_{2a}[H^+] + K_{2a}K_{1a}/[H^+]^2$$

The values of $\log \beta_2$, pK_{2a} and pK_{1a} and the associated thermodynamic functions corresponding to data at $30^\circ C$ are given in Table 1.

Spectral and magnetic properties of the Co(II), Ni(II) and Cu(II) complexes with the present ligand have been discussed in a separate communication¹. It was observed that an increase in polarity of the solvent medium caused very little or no change in the spectra

of the Co(II) complex, $Co(BMPBz)_2$ or $Co(L)_2$. But Ni(II) and Cu(II) complexes, viz. $Ni(BMPBz)_2$ or $Ni(L)_2$ and $Cu(BMPBz)_2 \cdot 2H_2O$ or $Cu(L)_2 \cdot 2H_2O$ tended to show increasing octahedral behaviour with increase in polarity of solvents. The behaviour of the Co(II) complex was very close to those of octahedral complexes of this metal ion. The ligand BMPBzH, therefore, functions as a tridentate (N,N,S) ligand for Co(II) and as a bidentate ligand for Ni(II) and Cu(II). This is also evident from the higher values of stability constants of the Co(II) complexes compared with those of the Ni(II) complexes, contrary to the general trend as given by Irving and Williams¹⁸. The higher stability of Co(II) complexes as compared with that of Ni(II) complexes is due partly to the favourable entropy change arising out of tridentate (N,N,S) chelation by the ligand in the case of Co(II) as against bidentate (N,N) chelation in the case of Ni(II) and partly due to the pronounced sigma-basicity and pi-acidity of the sulphur (CH_3-S-) donor atom. The unusual order of stability constants, $K_2 > K_1$, in the case of Co(II) is also a consequence of the metal $\rightarrow$ ligand charge-transfer through $Co(II) \rightarrow S-CH_3$ pi-bonds, where the pronounced sigma donor and pi-acceptor ability of the first ligand molecule facilitates the association of the second ligand molecule and thereby makes $K_2 > K_1$. Similar effects were observed for the Ni(II) complexes of penicillamine and cysteine¹⁶ and N-benzenesulphonyl-L-cysteine¹⁷. Deprotonation of coordinated imidazole rings in the presence of metal ions is a direct consequence of N(imidazole) $\rightarrow$ metal sigma bonding. Therefore, for higher values of the

stability constants (K_1 and K_2), higher values of the deprotonation constants K_{2a} and K_{1a} for the complexes are expected. This sequence was found to follow for Ni(II) and Zn(II) complexes and also for Co(II) and Zn(II) complexes. But contrary to this expectation, K_{2a} and K_{1a} values for Co(II) complexes were often found to be lower than those for the Ni(II) complexes, though K_1 and K_2 values for Co(II) complexes were always higher than those for the Ni(II) complexes. Pronounced sigma-basicity and pi-acidity of the softer sulphur donor atom probably weaken the N(imidazole)→Co(II) sigma bonding and hence lower the values of K_{2a} and K_{1a} for the cobalt complex. Comparatively higher stability of Zn(II) complex also suggests tridentate (N,N,S) chelation by the ligand as in the case of Co(II). Stability constant (β_2) of the copper(II) complex $\text{Cu}(\text{LH})_2^{2+}$ could not be compared with ($K_1 K_2$) values of ML_2 ($\text{M} = \text{Co}, \text{Ni}, \text{Zn}$) as these constants represent different equilibria. Same is true for the deprotonation constants K_{2a} and K_{1a} . The deprotonation of the complex $\text{Cu}(\text{LH})_2^{2+}$ ion involved loss of the sulphonamide protons while deprotonation of the complexes ML_2 ($\text{M} = \text{Co}, \text{Ni}, \text{Zn}$) involved loss of protons from the imidazole ring; of course, both were the consequences of N→metal sigma bonding. Due to the tendency of Cu(II) and Ni(II) complexes for having square planar geometry, the association of H_2O molecules of OH^- ions to $\text{M}(\text{N},\text{N})_2$ complexes [$\text{M} = \text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$] will be very weak; consequently, the possibility of deprotonation of coordinated water in the Cu(II) and Ni(II) complexes of the present ligand will be very low. In the $\text{M}(\text{N},\text{N},\text{S})_2$ complexes [$\text{M} = \text{Co}(\text{II})$ and $\text{Zn}(\text{II})$] there is no room for coordination of H_2O molecules or OH^- ions. Therefore, release of two protons by the complexes ML_2 [$\text{M} = \text{Co}(\text{II}), \text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$] and $\text{Cu}(\text{LH})_2^{2+}$ results because of the deprotonation of coordinated ligand, L^- ion or LH respectively but not due to the formation of hydroxo complexes from ML_2 or $\text{Cu}(\text{LH})_2^{2+}$.

Entropy changes accompanying complex formation reactions (3), (4) and (15), (16) were positive as a consequence of chelate ring formation. Entropy

changes for the deprotonation steps (5) and (6) were small negative or zero due to the formation of charged species $\text{M}(\text{H}_{-1}\text{L})(\text{L})^-$ and $\text{M}(\text{H}_{-1}\text{L})_2^{2-}$ around which arrangement of solvent molecules is facilitated. Comparatively smaller positive entropy change accompanying the formation of the complex $\text{Cu}(\text{LH})_2^{2+}$ ion arises probably due to retention of the overall positive charge of the metal ion in the complex. Deprotonation of $\text{Cu}(\text{LH})_2^{2+}$ ion (Eqs 17, 18) involves reduction or neutralization of charge on the complex; consequently, entropy change is positive due to release of solvent molecules associated with the ions $\text{Cu}(\text{LH})_2^{2+}$ and $\text{Cu}(\text{L})(\text{LH})^+$.

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