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Equilibrium studies on mixed ligand complex formation of Co(II), Ni(II), Cu(II) and Zn(II) with *N*-(2-hydroxybenzyl)-L-histidine (H_2hb-L-his) and typical N,N donor ligands: Crystal structure of [Ni(hb-L-his)(bipyridine)] · H_2O complex

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Abstract

Equilibrium study on complex formation of Co(II), Ni(II), Cu(II) and Zn(II), hereafter M(II), with the quadridentate (O^-, N, O^-, N) donor ligand, *N*-(2-hydroxybenzyl)-L-histidine (H_2hb-L-his, hereafter H_2L), in the absence and in the presence of typical (N, N) donor bidentate ligands, 1,10 phenanthroline(phen), 2, 2′-bipyridine(bipy), ethylenediamine(en), hereafter B, in aqueous solution at 25 ± 1 °C was done at a fixed ionic strength, $I = 0.1$ mol dm^{-3} ($NaNO_3$) by combined pH-metric, UV–Vis and EPR measurements provide evidence for the formation of mononuclear and dinuclear binary and mixed ligand complexes of the types: M(L), $M(L)_2^{2-}$, $M_2(L)^{2+}$, $M_2(H_{-1}L)^+$, M(L)(B), $(B)M(H_{-1}L)M(B)^+$. The imidazole moiety of the ligand is found to act as a bridging bidentate ligand in the dinuclear $M_2(L)^{2+}$, $M_2(H_{-1}L)^+$ and $(B)M(H_{-1}L)M(B)^+$ complexes, using its N_3 atom and N_1–H deprotonated moiety. Stability constants of the complexes provide evidence of discrimination of Cu(II) from the other M(II) ions by this ligand. Solid complexes: $[Ni(L)(H_2O)_2]$ (**1**), $[Cu(L)(H_2O)]$ (**2**), and $[Ni(L)(bipy)] \cdot H_2O$ (**3**) have been isolated and characterized by various physicochemical studies. Single crystal X-ray diffraction of the ternary complex, **3**, shows an octahedral $[(O^-,N,N,O^-)(N,N)]$ geometry with extensive π–π stacking of the aromatic rings and H-bonding with imidazole (N_1–H), secondary amino N-atom, the lattice H_2O molecule, and the carboxylate and phenolate O-atoms.

Keywords: *N*-(2-hydroxybenzyl)-L-histidine; Metal(II) complexes; Stability constants; Crystal structure

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1. Introduction

Schiff bases derived from amino acids and aldehydes provide useful models for enzymic processes, viz., *transamination* and *racemisation* reactions of amino acids [1]. Reduced products of such Schiff bases, because of greater flexibility arising from reduction of the azo methyne (–CH=N–) group, appear to serve as better models in this respect. Structural studies on the metal complexes of reduced Schiff base ligands, derived from various amino acids and salicylaldehyde, are well documented [2], but studies on the complex formation equilibria of metal ions with such ligands are limited [3]. Recently, structural topologies of some binary and mixed ligand complexes of Cu(II) with a series of *N*-(2-hydroxybenzyl) amino acid ligands, obtained on reduction of the Schiff bases derived from salicylaldehyde and various amino acids, viz., L-alanine [2d,2e], L-valine [2f] and other amino acids, viz., glycine [2g], β-alanine [2h], 4-aminobutyric acid [2i], 1-aminomethanesulfonic acid and 2-aminoethanesulfonic acid [2j], 1-amino-1-cyclopropanecarboxylic acid [2k], have been extensively investigated by Vittal and coworkers. In this paper, we report the equilibrium studies on the complex

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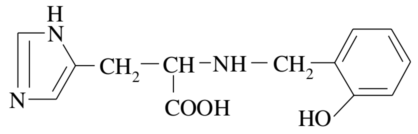


H_2hb-L-his (H_2L)

Scheme 1.

formation of Co(II), Ni(II), Cu(II) and Zn(II) with the ligand *N*-(2-hydroxybenzyl)-L-histidine (H_2hb-L-his, hereafter H_2L) (Scheme 1) in the absence and in the presence of typical (N,N) donor bidentate ligands, viz., ethylenediamine (en), 2,2′-bipyridine(bipy) and 1,10-phenanthroline(phen). The ligand (H_2L) is obtained by reducing the Schiff base derived from L-histidine and salicylaldehyde with sodium borohydride. Binary complexes of Ni(II) and Cu(II) with H_2L and a ternary Ni(II) complex formed with it in the presence of bipy as the auxiliary ligand have been isolated and characterized. The ligand H_2L appears as an unusual amino acid, containing an imidazole moiety and a phenolic group in addition to the amino and the carboxylate functions. The ligand ion, L^{2-}, provides (O^-, N, O^-, N) quadridentate chelation, using the carboxylate oxygen atom, the secondary amino nitrogen atom, the phenolate oxygen atom, and the imidazole nitrogen atom, creating a coordination environment, involving a combination of hard, border line and soft ligand atoms. The coordinated ligand ion, $H_{-1}L^{3-}$, provides quinquodentate (O^-, N, O^-, N, N^-) chelation in dinuclear binary and ternary complexes using the deprotonated N_1–H moiety of the imidazole as the fifth coordinating site. The ligand has a tendency to form H-bonded network due to the presence of a complementary H-bond donor and acceptor groups within the same molecule.

2. Experimental

All the reagents other than the ligand (H_2L) were obtained from commercial sources as A.R. grades and were used without further purification.

2.1. Synthesis

2.1.1. N-(2-hydroxybenzyl)-L-histidine, H_2hb-L-his $0.5H_2O$ ($H_2L \cdot 0.5H_2O$)

The ligand $H_2L \cdot 0.5H_2O$ was prepared by reducing the Schiff base obtained from the condensation reaction of L-histidine with salicylaldehyde with sodium borohydride following the reported procedure [2b]. Its purity was checked from its m.p., elemental analysis, IR and ^1H NMR spectral data.

2.1.2. $[Ni(L)(H_2O)_2]$ (**1**)

To a solution of a mixture of $H_2L \cdot 0.5H_2O$ (270 mg, 1 mmol) and KOH (112 mg, 2 mmol) in 1:1 methanol:water (20 ml) was added a solution of $Ni(NO_3)_2.6H_2O$ (291 mg, 1 mmol) in methanol. The resulting blue reaction mixture was stirred for one hour, filtered and allowed to stand in air at room temperature for slow evaporation. Bluish violet crystals of complex **1** separated within a few days. The crystals were filtered and washed with water (yield, 208 mg, ca. 70%). *Anal.* Calc. for $C_{13}H_{17}NiN_3O_5$: C, 44.1; H, 4.8; N, 11.8; Ni, 16.6. Found: C, 43.9; H, 4.6; N, 11.6; Ni, 16.4%. λ_{max}/kK (H_2O) (ε/mol^{-1} dm^3 cm^{-1}) 11.1 (144.5), 18.1 (100.2), 27.5 (60.7). IR (KBr disk, ν/cm^{-1}): ν(OH) 3579; ν_{as} (COO) 1579; ν(C–N) 1457, ν_s (COO) 1391, ν(phenolic, C–O) 1250. μ_{eff}/BM (298 K) 2.97.

2.1.3. $[Cu(L)(H_2O)]$ (**2**)

To a hot slurry of freshly precipitated alkali free $Cu(OH)_2$ (200 mg, ~2 mmol), $H_2L \cdot 0.5H_2O$ (540 mg, ~2 mmol) was added and the mixture was digested on a steam bath for 10 min. $Cu(OH)_2$ gradually dissolved giving a green solution, which was filtered hot and allowed to stand in air. Green crystals of complex **2** separated out within a few minutes (yield, 125 mg, ca. ~65%). *Anal.* Calc. for $C_{13}H_{15}CuN_3O_4$: C, 45.8; H, 4.4; N, 12.3; Cu, 18.6. Found: C, 45.4; H, 4.2; N, 12.1; Cu, 18.3%. λ_{max}/kK (H_2O) (ε/mol^{-1} dm^3 cm^{-1}) 15.1(79.6), 25.7 (346.4). IR (KBr disk, ν/cm^{-1}): ν(OH) 3563; ν_{as} (COO) 1590; ν(C–N) 1482, ν_s(COO) 1385, ν(phenolic, C–O) 1252. μ_{eff}/BM (298 K) 1.88.

2.1.4. $[Ni(L)(bipy)] \cdot H_2O$ (**3**)

To a solution of a mixture of $H_2L \cdot 0.5H_2O$ (270 mg, 1 mmol) and $NaHCO_3$ (168 mg, 2 mmol) in water (20 ml) was added a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (291 mg, 1 mmol) in water. The mixture was refluxed for 30 min. To the refluxing reaction mixture, 2,2′-bipyridine (156 mg, 1 mmol) in ethanol (15 ml) was added dropwise. The resulting greenish brown solution was refluxed for 3 h, filtered hot and the volume of the filtrate was reduced by evaporation on a steam bath. Brown needle shaped single crystals of complex **3**, suitable for X-ray diffraction, appeared on standing the reaction mixture overnight at room temperature (yield, 205 mg, ca. 70%). *Anal.* Calc. for $C_{23}H_{23}NiN_5O_4$: C, 56.1; H, 4.6; N, 14.2; Ni, 11.9. Found: C, 55.8; H, 4.4; N, 14.1; Ni, 11.7%. λ_{max}/kK (H_2O) (ε/mol^{-1} dm^3 cm^{-1}) 8.7 (26.5), 10.4 (30.4), 18.6 (24.6). IR (KBr disk, ν/cm^{-1}): ν(OH) 3517; ν_{as}(COO) 1598; ν(C–N) 1473, ν_s(COO) 1395, ν(phenolic, C–O) 1207. μ_{eff}/BM (298 K) 2.91.

2.2. Analytical and physicochemical measurements

2.2.1. Crystal structure determination of complex 3

Single crystal X-ray diffraction data for complex **3** were recorded with Mo Kα radiation ($\lambda = 0.71073$ Å) using the MAR research Image Plate System. The crystal was positioned at 70 mm from the image plate. 95 frames were measured at 2° intervals with a counting time of 2 min. Data analyses were carried out following the procedures [4–6] described earlier [7a]. The summary of crystallographic data and structure refinement parameters is presented in Table 1, and some selected bond lengths and bond angles in the structures (Figs. 1 and 2) are shown in Tables 2 and 3.

2.2.2. Potentiometric investigations

Equilibrium study for the determination of proton–ligand and metal(II)–ligand constants involved pH-metric titration of series of solutions, each of initial volume 25 cm^3, containing 1×10^{-2} mol dm^{-3} HNO_3 and known amounts (1×10^{-3} to 5×10^{-3} mol dm^{-3}) of the ligand $H_2L \cdot 0.5H_2O$ in its protonated form (H_3L^+) (NO_3^-) in the absence and in the presence of known amounts (1×10^{-3} to 2×10^{-3} mol dm^{-3}) of metal(II) nitrates and known amounts (1×10^{-3} to 2×10^{-3} mol dm^{-3}) of H_2B^{2+} (B = en, bipy, phen) in the form of nitrate salts, maintaining the metal(II):H_2L:B molar ratios of 1:1:1 and 2:1:2 at a fixed ionic strength, $I = 10^{-1}$ mol dm^{-3} ($NaNO_3$) at 25 ± 1 °C (thermostated). Experimental details and methods of calculation of the equilibrium constants (Tables 4 and 5) were the same as described earlier [7].

Table 1
Summary of crystal data, data collection and structural refinement parameters for complex [Ni(L)(bipy)] · H_2O (**3**)

Empirical formula	$C_{23}H_{23}N_5O_4Ni$
Formula weight	492.18
Crystal system	monoclinic
Space group	$P2_1$
a (Å)	9.483(10)
b (Å)	7.301(9)
c (Å)	16.466(17)
β (°)	100.05(1)
V (Å^3)	1123(2)
Z	2
d_{calc} (g cm^{-3})	1.456
Independent, observed reflections ($I > 2\sigma(I)$)	3936, 3460
R_1, $wR(F^2)$	0.0465, 0.0926
Maximum, minimum residual density (e/Å^3)	0.205, −0.309

2.2.3. Spectral measurements and thermal analysis

Experimental procedure for collecting the data on elemental analysis, TG/DTA, IR, and UV–Vis spectra were the same as described earlier [7,8]. Room temperature magnetic susceptibilities of complexes **1**, **2** and **3** were measured in polycrystalline state on a PAR 155 sample vibrating magnetometer. Solutions of concentrations comparable to those used in the potentiometric measurements were used for EPR and UV–Vis measurements. The EPR spectra of Cu(II)–H_2L and Cu(II)–H_2L–B mixtures at pH values corresponding to the concentration maxima of the binary and ternary complex species, Cu(L) and Cu(L)(B), respectively, as observed in the species distribution curves (Figs. 3 and 4) were run on a Varian model E-112 spectrometer (X-band) in H_2O–ethylene glycol at LNT using DPPH ($g = 2.0036$) as the standard in the field range of 1200–5200 G.

3. Results and discussion

3.1. Physicochemical studies on solid complexes

The IR bands in the range 3517–3579 cm^{-1} may be assigned to ν(OH) of lattice water molecules in compounds

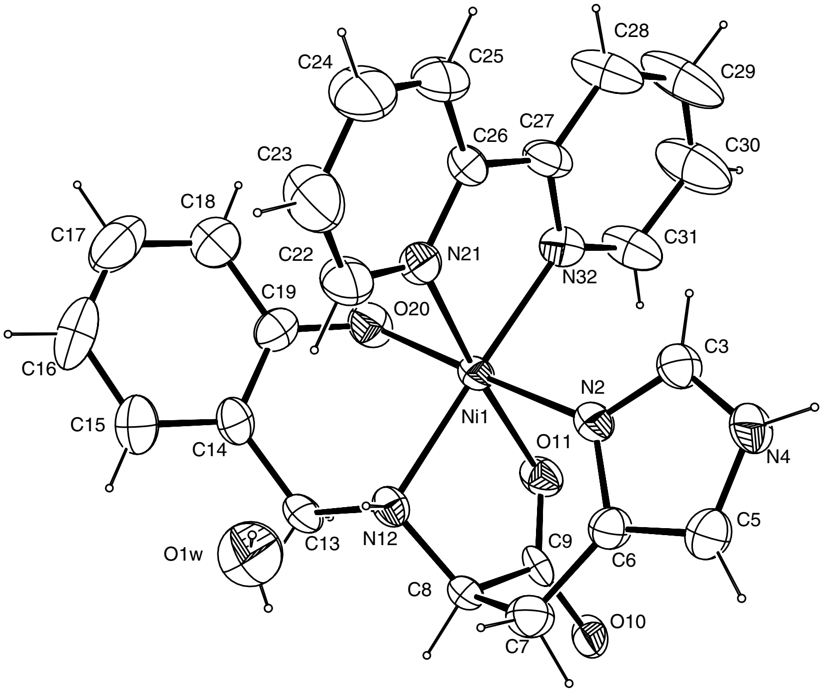


Fig. 1. ORTEP view of complex **3** with atom labeling scheme. Thermal ellipsoids are shown at 50% probability.

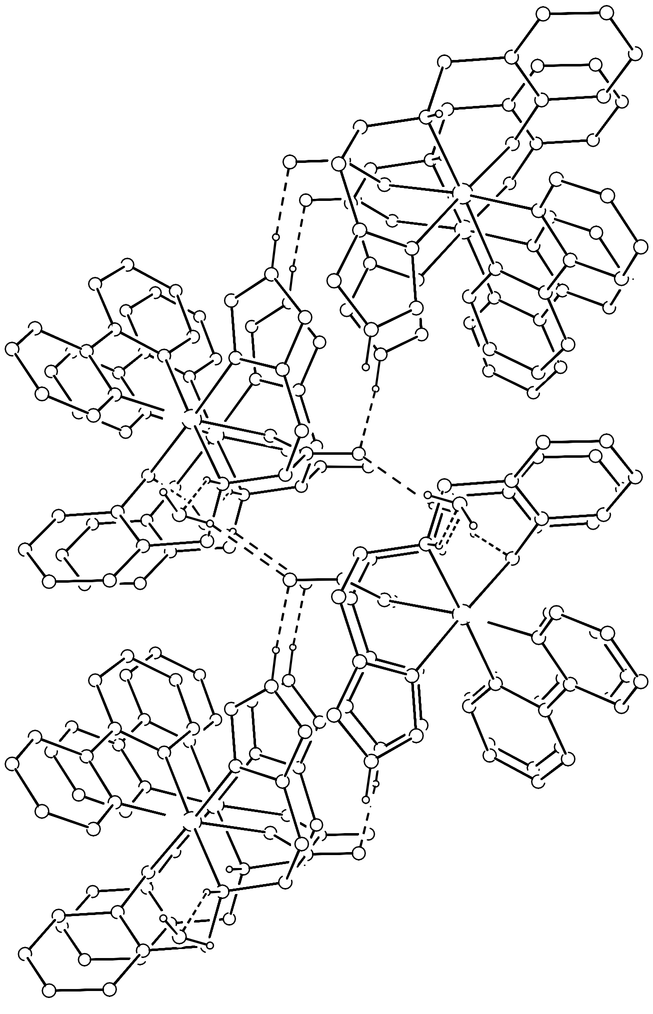


Fig. 2. Hydrogen bonded packing of **3**.

Table 2
Some selected bond distances (Å) and bond angles (°) of complex [Ni(L)(bipy)] · H_2O (**3**)

Ni(1)–N(32)	2.073(5)	Ni(1)–O(20)	2.078(4)
Ni(1)–N(2)	2.130(4)	Ni(1)–N(12)	2.089(4)
Ni(1)–O(11)	2.110(4)	Ni(1)–N(21)	2.093(4)
O(11)–Ni(1)–O(20)	94.50(13)	O(20)–Ni(1)–N(32)	88.25(14)
O(11)–Ni(1)–N(2)	86.49(12)	N(2)–Ni(1)–N(12)	88.38(13)
O(11)–Ni(1)–N(12)	79.85(12)	N(2)–Ni(1)–N(21)	88.19(14)
O(11)–Ni(1)–N(21)	174.34(13)	N(2)–Ni(1)–N(32)	90.44(13)
O(11)–Ni(1)–N(32	98.94(13)	N(12)–Ni(1)–N(21)	101.93(15)
O(20)–Ni(1)–N(2)	178.47(13)	N(12)–Ni(1)–N32)	178.36(13)
O(20)–Ni(1)–N(12)	92.94(13)	N(21)–Ni(1)–N(32)	79.16(15)
O(20)–Ni(1)–N(21)	90.77(14)		

1–3 [9]. The presence of lattice water is further supported by the weight loss percents observed in the temperature range 40–220°C. The asymmetric ν_{as}(COO) and the symmetric ν_s(COO) stretching bands of the complexes fall in the regions 1579–1598 and 1385–1395 cm^{-1}, respectively. The difference between ν_{as}(COO) and ν_s(COO) stretching frequencies ($\sim$200 ± 5 cm^{-1}) suggests only terminal mode of coordination by the carboxylate groups [10,11]. The strong band around 1273 cm^{-1} due to the ν(C–O) phenolic in the free ligand shifts to lower frequencies in all these complexes, suggesting coordination of metal by the phenolic oxygen atom.

The anhydrous products resulting from thermal dehydration of **1–3** between 40 and 200 °C undergo two consecutive pyrolytic steps between the temperature ranges 220 and 550 °C, of which the first step (200–360 °C) corresponds to dissociation of the imidazole moiety from the ligand, and the second step (360–550 °C) corresponds to pyrolysis of the resulting product to form metallic oxides, MO.

Electronic spectra of the Ni(II) complexes **1** and **3** show three well resolved bands (11.1, 18.1, 27.4 kK and 8.7, 10.4 and 18.6 kK, respectively), which on an octahedral geometry correspond to the transitions: ν_1 [$^3A_{2g} \rightarrow {}^3T_{2g}$], ν_2 [$^3A_{2g} \rightarrow {}^3T_{1g}(F)$], ν_3 [$^3A_{2g} \rightarrow {}^3T_{1g}(P)$], respectively. In both complexes **1** and **3**, lowering of Racah parameter (B) of Ni^{2+} ion from 1.1 kK in free ion to 0.8 kK and 0.2 kK (B') in complexes **1** and **3**, respectively, indicates delocalization of metal ion dπ-electrons over to the aromatic π-systems of the coordinated ligands, viz., imidazole moiety in **1** and both imidazole and bipy moieties in **3**. Electronic spectra of the Cu(II) complex, **2**, show two peaks. A broad band centered at 15.1 kK indicates a distorted octahedral geometry of the complex and a sharp band at 25.7 kK may be assigned to the charge transfer transition from filled σphenolate-O atom to partly filled or vacant $\sigma^*(x^2 - y^2)$ orbital of Cu(II) ion [12].

Room temperature magnetic moment (μ_{eff}) values of complexes **1–3** are close to the spin only values for Ni(II) and Cu(II) ions.

3.2. Description of crystal structure of complex 3

ORTEP view of complex **3** with the atom numbering scheme is shown in Fig. 1. Geometry around the Ni(II) ion in **3** is distorted octahedral with the carboxylate oxygen atom (O11), the phenolate oxygen atom (O20), the secondary amino nitrogen atom (N12) and the pyridine type

Table 3
Hydrogen bond distances (Å) and bond angles (°) of complex [Ni(L)(bipy)] · H_2O (**3**)

D–H	d(D–H)	d(H···A)	∠DHA	d(D···A)	A	Symmetry
O1W–H1W	0.71(7)	2.29(7)	155(8)	2.950(6)	O10	$[1 - x, -1/2 + y, 1 - z]$
O1W–H2W	0.94(6)	1.83(6)	166(6)	2.746(6)	O20	$[x, -1 + y, z]$
N4–H4	0.860(6)	1.904(5)	159.7(4)	2.726(6)	O10	$[2 - x, -1/2 + y, 1 - z]$
N12–H12	0.910(5)	2.138(6)	153.0(3)	2.978(7)	O1W	

Table 4
Proton–ligand constants of H_2L and B ligands

Constants	Ligands			
	H_3L^+	H_2phen^{2+}	H_2bipy^{2+}	H_2en^{2+}
$\log\beta_{010\text{-}3}$	24.43			
$\log\beta_{010\text{-}2}$	18.50			
$\log\beta_{010\text{-}1}$	10.38			
$\log\beta_{001\text{-}2}$		6.86	5.55	16.99
$\log\beta_{001-1}$		4.96	4.23	9.89

[$I = 10^{-1}$ mol dm^{-3} ($NaNO_3$); 25 ± 1 °C].

Table 5
Stability constants of M(II)-L binary and M(II)-L-B(phen, bipy, en) ternary complexes (M = Co, Ni, Cu and Zn)

Constants	B	Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}
$\log\beta_{1100}$		9.36	11.37	15.44	9.52
$\log\beta_{1200}$		13.61	14.26	17.80	13.55
$\log\beta_{2100}$		13.63	16.03	18.83	13.07
$\log\beta_{2101}$		4.23	7.23	11.75	3.73
$\log K_d$		−12.50	−12.76	−9.68	−11.44
$\log\beta_{1010}$ [15]	phen	7.83	8.64	9.14	6.22
	bipy	6.06	7.13	7.80	5.15
	en	5.62	6.96	10.44	5.61
$\log\beta_{1110}$	phen	17.80	19.80	24.44	15.41
	bipy	15.93	18.17	23.01	14.28
	en	15.42	17.94	25.36	14.76
$\Delta\log K_M$	phen	−0.28	−0.21	−0.14	−0.30
	bipy	−0.38	−0.33	−0.23	−0.43
	en	−0.45	−0.39	−0.52	−0.49
$\log\beta_{2121}$	phen	18.90	22.06	27.46	16.34
	bipy	17.56	18.49	26.35	15.15
	en	16.13	18.32	26.12	14.71

Limits of error: ±0.02–0.05 in log scale.
Temp. 25 ± 1 °C; ionic strength $I = 10^{-1}$ mol dm^{-3} ($NaNO_3$) in aqueous solution.

nitrogen atom (N2) of the imidazole moiety of the ligand dianion, (L^{2-}), coordinating four positions, leaving two *cis*-positions vacant for coordination by the two nitrogen atoms (N21 and N32) of the bipyridine ligand. Four donor atoms [O20, N12, N2, N32] define a mean equatorial plane, P1 [deviations of −0.0173 and −0.0172 Å for O20 and N2 to 0.0170 and 0.0175 Å for N12 and N32]. The other two planes formed by [O20, N21, N2, O11] and [N12, N21, N32, O11] are almost perpendicular to P1 forming dihedral angles of 79.55° and 88.91°, respectively, with P1, and these two planes are also perpendicular to each other forming a dihedral angle of 88.58°. One of the two five-membered chelate rings, Ni1–O11–C9–C8–N12, has half chair conformation having the puckering parameters [13], $q_2 = 0.472(3)$ Å; $\varphi_2 = 343.1(5)°$. The other five-membered ring constructed by Ni1–N21–C26–C27–N32 is approximately planar with a N–C–C–N torsion angle of 0.97°. The six-membered chelate rings Ni1–N2–C6–C7–C8–N12 and Ni1–O20–C19–C14–C13–N12 have twist boat conformation with puckering parameters $q_2 = 0.460(4)$, $q_3 = -0.487(4)$ Å and $\varphi_2 = 98.9(5)°$ and boat conformation with puckering parameters $q_2 = 0.814(4)$, $q_3 = 0.008(4)$ Å and $\varphi_2 = 235.4(3)°$, respectively. The carboxylate oxygen atom (O10), the phenolate oxygen atom (O20), the H-atoms attached to the pyrrole type nitrogen atom N(4) of the imidazole moiety, and the secondary amino nitrogen atom (N12) and one lattice H_2O molecule are involved in extensive H-bonding (Fig. 2).

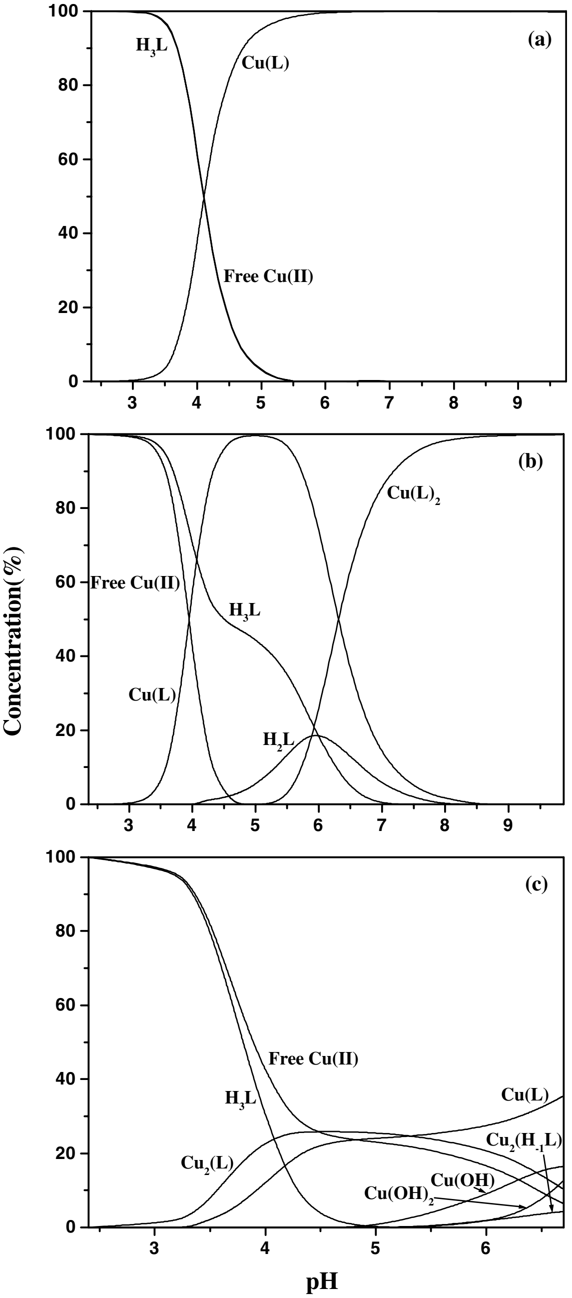


Fig. 3. Species distribution curves of (a) 1:1, (b) 1:2 and (c) 2:1 Cu(II)–H_2L systems.

3.3. Equilibrium study

3.3.1. Protonation–deprotonation equilibria of the ligand H_2L

The ligand (H_2L) is sparingly soluble in water and in common organic solvents. It is brought into solution as

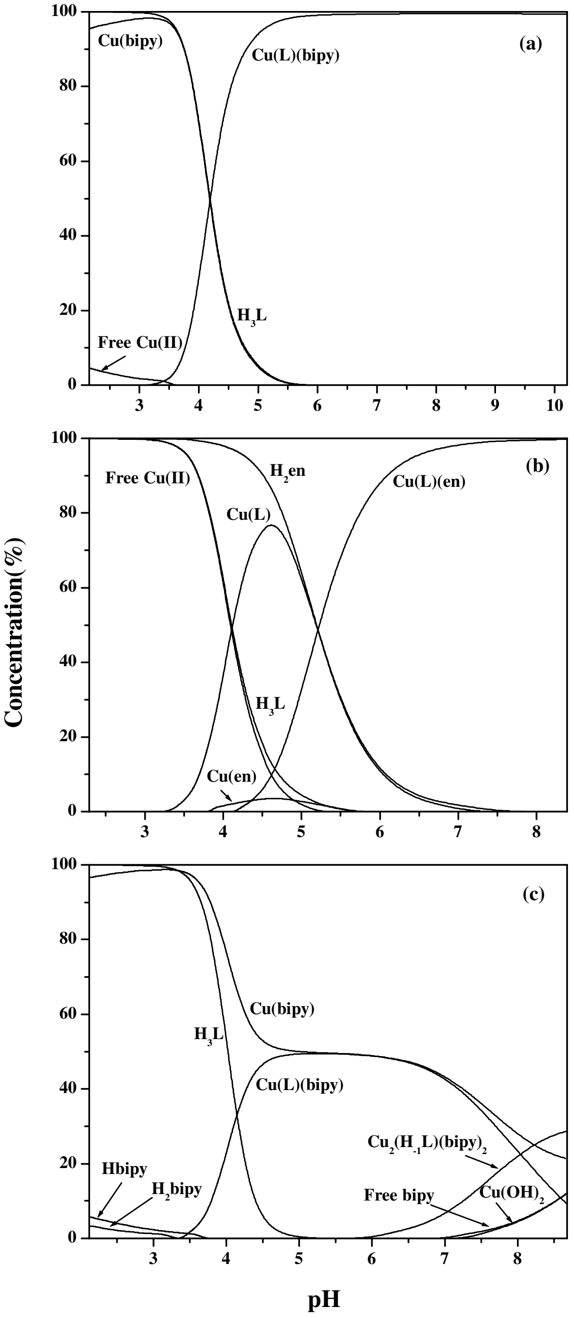


Fig. 4. Species distribution curves of (a) 1:1:1 Cu(II)–H_2L-bipy, (b) 1:1:1 Cu(II)–H_2L-en and (c) 2:1:2 Cu(II)–H_2L-bipy systems.

its mono nitrate salt form, $H_2L \cdot HNO_3$ [i.e., (H_3L^+) $(NO_3{}^-)$]. At pH $\leqslant 2$ its cation, H_3L^+, titrates as a triprotic acid in the pH range 2–11, due to successive deprotonation of the –COOH group (pH 2–6) followed by deprotonation of the amino–N^+H and the –OH protons in the successive steps.

3.3.2. Metal (II)–ligand equilibria

The overall stability constants (β_{pqrs}) of the generalized complex species, $M_pL_qB_r(OH)_s$, may be defined according to

$$pM + qL + rB + sOH \rightleftharpoons M_pL_qB_r(OH)_s \tag{1}$$

$$\beta_{pqrs} = \frac{[M_pL_qB_r(OH)_s]}{[M]^p[L]^q[B]^r[OH]^s}, \tag{1a}$$

where p, q, r and s are stoichiometric numbers. p, q and r are positive integers or zero. s is a negative integer for a protonated species, zero for a neutral species and positive for a hydroxo or a deprotonated species. Charges are omitted for simplicity. β_{pqrs} values have been calculated by analyzing the pH titration data of the metal–ligand mixtures using the computer program, SCOGS [14]. The other relevant constants may be calculated from the β_{pqrs} values using appropriate relations. Preliminary values of β_{1010}, obtained from literature [15], have been subjected to computer refinement using the SCOGS program [14] with the pH titration data of the 1:1, 1:5 and 1:10 M(II):$BH_2{}^{2+}$ mixtures and the values corresponding to lowest standard deviations have been accepted. For some of the systems, such as Co(II)–phen, the preliminary β_{1010} value has been calculated from the corresponding value of Ni(phen), assuming as a first approximation, the difference between the $\log\beta_{1010}$ values of Ni(phen) and Co(phen) to be same as that between Ni(bipy) and Co(bipy), for which literature values of β_{1010} are available [15]. β_{1100}, β_{1200}, β_{2100}, β_{1010}, β_{1110} and β_{2121} values are obtained as computer output, from which the reprotonation constant $\Delta\log K_M$ [16] for mixed-ligand complexes may be calculated using the relation:

$$\Delta\log K_M = \log\beta_{1110} - \log\beta_{1100} - \log\beta_{1010}. \tag{2}$$

3.3.2.1. Binary M(II):H_2L (1:1, 1:2 and 2:1) equilibria.

Complex formation equilibria in 1:1 metal(II):H_2L systems with all the four metal(II) ions (M = Co, Ni, Cu and Zn) start at pH 4–5. Binary 1:1 complexes, M(L), are the major metal containing species at pH < 7 (Fig. 3a). These are formed according to

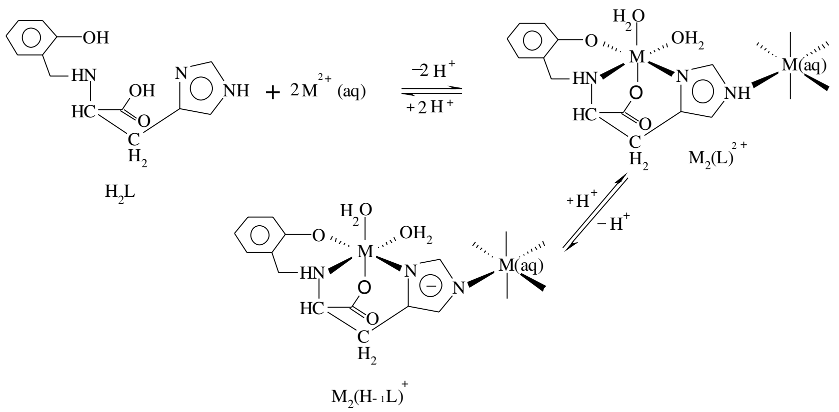
$$M^{2+} + H_3L^+ \rightleftharpoons M(L) + 3H^+ \tag{3}$$

Consequently, three moles of base per mole of M^{2+} are consumed in this pH range, since the buffer regions corresponding to all the three-steps of deprotonation of the ligand are lowered in the presence of M(II) ions. 1:1 Cu(II)–H_2L mixture at pH ~ 6 shows λ_{max} at 25.3 and 14.6 kK and its EPR spectrum gives $g_\parallel = 2.1276$, $A_\parallel/G = 48$, indicating a octahedral $[Cu(II)(O)_4(N)_2]$ geometry [17], in which the carboxylate oxygen atom, the phenolate oxygen atom, the amino nitrogen atom and the pyridine type nitrogen atom of the imidazole moiety of the ligand and two H_2O molecules coordinate the Cu(II) ion.

The speciation curves (Fig. 3b) of 1:2 M(II):H_2L mixtures show the formation of $M(L)_2{}^{2-}$ complexes at pH > 7.5 according to

$$M(L) + H_2L \rightleftharpoons M(L)_2{}^{2-} + 2H^+ \tag{4}$$

$$M(L) + HL^- \rightleftharpoons M(L)_2{}^{2-} + H^+ \tag{5}$$



Scheme 2.

$Cu(L)_2{}^{2-}$ ion (λ_{max}: 25.1 and 15.2 kK), which is the major metal containing species in the 1:2 Cu(II):H_2L system at pH > 8, is however formed according to

$$Cu(L) + H_3L^+ \rightleftharpoons Cu(L)_2{}^{2-} + 3H^+ \tag{6}$$

In the 2:1 M(II):H_3L^+ systems, the imidazole bridged binuclear complexes, $M_2(L)^{2+}$, appear at pH > 4 (Fig. 3c) according to

$$2M^{2+} + H_3L^+ \rightleftharpoons M_2(L)^{2+} + 3H^+ \tag{7}$$

Concentration maximum of the dinuclear complex, $Cu_2(L)^{2+}$ (λ_{max}: 32.8 and 14.2 kK), is observed at pH ~ 4. At higher pH values (pH > 5.5), the dinuclear complex species, $M_2(L)^{2+}$, decompose (equilibrium (8)) to produce the mononuclear M(L) complexes, and hydroxo species, M(OH), and it also undergo deprotonation (equilibrium (9)) of the imidazole (N_1–H) moiety (Scheme 2),

$$M_2(L)^{2+} + H_2O \overset{K_d}{\rightleftharpoons} M(L) + M(OH)^+ + H^+ \tag{8}$$

$$M_2(L)^{2+} \rightleftharpoons M_2(H_{-1}L)^+ + H^+ \tag{9}$$

The decomposition constant (K_d) and the deprotonation constant ($K^H_{M_2(L)}$) may be related to the experimentally determinable constants according to (8a) and (9a), respectively

$$\log K_d = \log \beta_{110} + \log \beta_{101} - \log \beta_{210}. \tag{8a}$$

$$\log K^H_{M_2(L)} = \log \beta_{2101} - \log \beta_{2100}. \tag{9a}$$

3.3.3. Ternary (1:1:1) and (2:1:2) M(II):H_2L:B equilibria (B = phen, bipy and en)

Speciation curves (Fig. 4a) of 1:1:1 M(II):H_3L^+:H_2B^{2+} (B = phen and bipy) ternary systems indicate the $M(B)^{2+}$ complexes as the major metal containing species at the start of the reaction (pH ~ 2). With rise of pH, these $M(B)^{2+}$ complexes react with H_3L^+ and H_2L to form the ternary M(L)(B) complexes according to equilibria:

$$\text{pH 2–5} \quad M(B)^{2+} + H_3L^+ \rightleftharpoons M(L)(B) + 3H^+ \tag{10}$$

$$\text{pH} > 5 \quad M(B)^{2+} + H_2L \rightleftharpoons M(L)(B)\ (B = \text{phen, bipy}) + 2H^+ \tag{11}$$

Free M^{2+} ions are practically non-existent from the very beginning of complex formation in these systems. The early stages (pH 2–5) of complex formation, in the ternary 1:1:1 M(II):H_3L^+:H_2en^{2+} systems (Fig. 4b) are dominated by the M(L) complexes, which may be formed according to:

$$M + H_nL \rightleftharpoons M(L) + nH \quad (n = 3, 2) \tag{12}$$

With rise of pH, these binary M(L) complexes take up the en ligand to form the ternary M(L)(B) complexes (B = en) above pH ~ 5 according to equilibrium:

$$M(L) + BH_n \rightleftharpoons M(L)(B)\ (B = en) + nH \quad (n = 2, 1) \tag{13}$$

Charges are not shown for simplicity. The ternary M(L)(en) complexes represent the major metal containing species above pH 8. Stability constants (Table 5) of the complexes fall in the usual order [18]: Co(II) < Ni(II) < Cu(II) > Zn(II)·$\Delta\log K_M$ (Table 5) values are found to be less negative than their statistical values [16], indicating favored formation of the ternary M(L)(B) complexes over the binary ones.

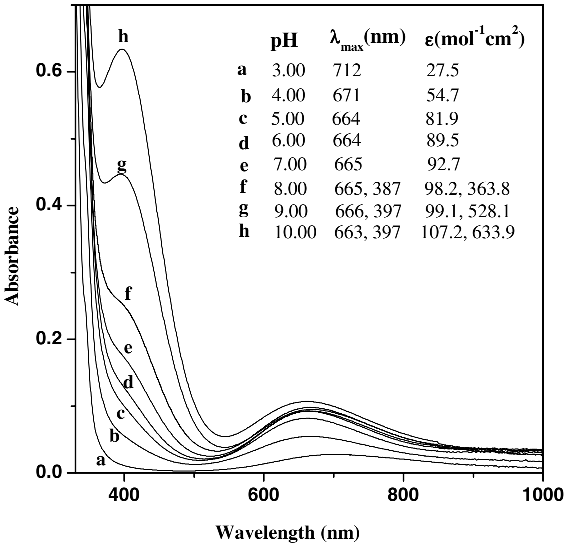
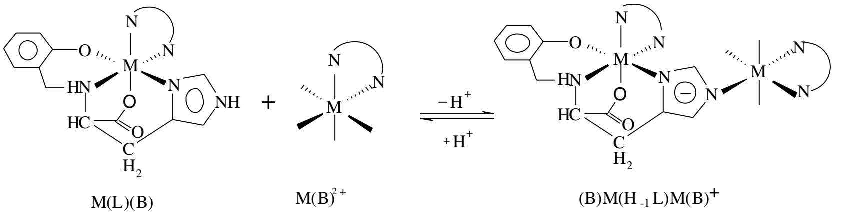


Fig. 5. Superimposed electronic spectral curves of 1:1:1 Cu(II):H_2L:phen mixtures at different pH values; [Cu(II)] 0.001 M in aqueous solution, $I = 0.1$ M ($NaNO_3$), $l = 1$ cm.



Scheme 3.

Concentration maxima of Cu(L)(B) complexes occur around pH 8. Electronic spectral band around 25.1 kK (Fig. 5) of 1:1:1 Cu(II):H_2L:phen mixture at this pH arises from the charge transfer transition from filled σ(O-phenolate) to vacant $\sigma^*(x^2-y^2)$ of Cu(II) ion [12]. The EPR spectra of the mixture at pH 8 give $g_\parallel = 2.1035$ and $A_\parallel/G = 68.6$, which are indicative of distorted octahedral $[Cu(II)(N)_4(O)_2]$ geometry [17], in which the carboxylate oxygen atom, the phenolate oxygen atom, the secondary amino nitrogen atom and the pyridine type nitrogen atom of the imidazole moiety of the ligand and two N-atoms of the (N,N) donor (B) ligands coordinate the Cu(II) ion. These modes of coordination of the L^{2-} and B ligands are evident from the crystal structure of the Ni(II) complex $[Ni(L)(bipy)] \cdot H_2O$ (**3**) (Fig. 1).

The speciation curves (Fig. 4c) of 2:1:2 M(II):-H_3L^{2+}:H_2B^{2+} mixtures at pH $\geqslant 5$ indicate the formation of imidazolate bridged dinuclear mixed ligand complexes of the types, $(B)M(H_{-1}L)M(B)^+$, according to the equilibrium:

$$M(L)(B) + M(B) \rightleftharpoons (B)M(H_{-1}L)M(B) + H \qquad (14)$$

in which one of the two M(II) ions may be coordinated by the carboxylate oxygen atom, the phenolate oxygen atom, the amino nitrogen atom and the pyridine type nitrogen atom of the imidazole moiety of the ligand $H_{-1}L^{3-}$ ion and two N-atoms of the (N,N) donor B ligands, and the other M(II) ion may be coordinated by the deprotonated (N_1–H) moiety of the imidazole ring, two N-atoms of the (N,N) donor B ligands and solvent H_2O molecules (Scheme 3). Consequently, the 2:1:2 Cu(II):H_2L:phen mixture shows a small blue shift of the absorption maxima with rise of pH from 5 to 8.5, indicating that a negatively charged (σ-basic and π-acidic) imidazolate moiety provides stronger ligand field than its neutral form [19].

With regards to the B ligands, the overall stability constants of the ternary complexes (i.e. $\log\beta_{1110}$ and $\log\beta_{2121}$) fall largely in the order: phen > bipy > en, since phen and bipy are σ-basic and π-acidic, whereas en is σ-basic only. Under exceptional cases, stability of ternary complexes with en as the secondary ligand is found to be slightly higher than those with bipy or phen, mainly because of greater flexibility of the chelate rings formed with the en ligand.

4. Conclusion

The ligand *N*-(2-hydroxybenzyl)-L-histidine (H_2L) shows ambidentism and discriminating power in its complexes with 3d M(II) ions. It coordinates as a diprotic (O^-, N, O^-, N) quadridentate ligand in mononuclear binary M(L) and mixed ligand M(L)(B) complexes (B = bipy, phen, en) using the carboxylate –O, secondary amino-N, phenolate-O and imidazole-(N_3) atoms. In dinuclear binary and mixed ligand complexes, it offers quinquodentate (O^-,N,O^-,N,N^-) coordination. The imidazole–N_1 atom coordinates the second metal ion through deprotonation of the N_1–H moiety. Because of a combination of hard (COO^-, O^--phenolate), borderline (–NH) and soft (imidazole N_3, N_1) donor groups within the same molecule, the ligand H_2L is able to discriminate Cu(II) from the other 3d M(II) ions (Co(II), Ni(II) and Zn(II)) in regard to stability of the complexes in solution.

5. Supplementary data

Crystallographic data for the structural analysis of the complex **3** have been deposited with the Cambridge Crystallographic Data Centre, with CCDC No. 290615. Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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