Complexation of 4-Dimethylamino benzilidene(N-benzoyl)glycyl Hydrazone with Ni²⁺, Cu²⁺ and Cd²⁺ Ions and their Potentiometric Studies in Aqueous-Dioxane and Aqueous-Micellar Media

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4-Dimethylamino benzilidene (N-benzoyl) glycyl hydrazone (HL) was prepared by the condensation of 4-dimethylamino benzaldehyde with N-benzoyl glycine hydrazide. Ni(II), Cu(II) and Cd(II) complexes of HL were synthesized and characterized based on the elemental analysis, conductivity, magnetic and spectral data. Protonation constant of the hydrazone and formation constants of the complexes have been determined potentiometrically at ionic strength 0.1 M KNO₃ at different temperatures 17, 27 and 37 ºC in aqueous-dioxane and aqueous-micellar media. A single inflection in the potentiometric titration curves of the ligand indicates the presence of only one dissociable proton in the ligand. pH-metric and elemental analysis data show that the ligand forms only 1:1 metal-ligand complexes with Ni²⁺, Cu²⁺ and Cd²⁺ ions. The presence of the anionic and non-ionic surfactants in the medium decreases the protonation constant of HL and formation constant of the complexes. This is due to the compartmentalization of the reacting species between the bulk water and the micellar pseudophase. Thermodynamic parameters such as changes in free energy (ΔG), entropy (ΔS) and enthalpy (ΔH) associated with protonation of HL and formation of M(II)-HL complexes in different media are calculated and discussed.

Key Words: Potentiometric studies, 4-Dimethylamino benzilidene-(N-benzoyl)glycyl hydrazone, Protonation and stability constants, Micellar media.

INTRODUCTION

Metal complexes of Schiff bases have been the subject of intensive research because they not only have interesting spectral and magnetic properties, but they also possess a diverse spectrum of biological and pharmaceutical activities[1-6]. A literature survey reveals that most of the studies on the binary and ternary complexes of transition metal ions with a number of Schiff bases are carried out in aqueous or aqueous-organic or mixed organic solvent media and studies of such reactions in micellar media are considerably less. It is despite the fact that many chemical reactions are reported[7-11] to be affected by the presence of micelles in the systems. The solubilising and compartmentalizing actions of micelles on the reactants strongly modify complex and acid-base equilibria, redox properties and reaction rates. It

has also been reported[9] that aqueous micellar media mimic 'organized assembly' akin to that present in a living cell. Since interactions of the metal ions with Schiff bases have served as model systems for the study of various biomolecules and metalloproteins, an insight into the protonation and formation equilibria of metal complexes of Schiff bases in micelles would, therefore, be helpful in understanding the metal-ligand equilibria associated with these ligands and give a wider range in biological application of the complexes[11-13]. Keeping these aspects in view and in continuation with our research work[14-16], we have synthesized a new Schiff base, 4-dimethylaminobenzylidene (N-benzoyl)glycyl hydrazone, HL (**1**) and Ni(II), Cu(II) and Cd(II) complexes and report here the structural characterization of these complexes. The present work also reports on the protonation constant of the Schiff base and the formation constants of the Ni(II), Cu(II) and Cd(II) complexes in aqueous and aqueous-micellar (anionic and nonionic) media and the thermodynamic parameters associated with the proton-ligand and metal-ligand formation reactions in different media.
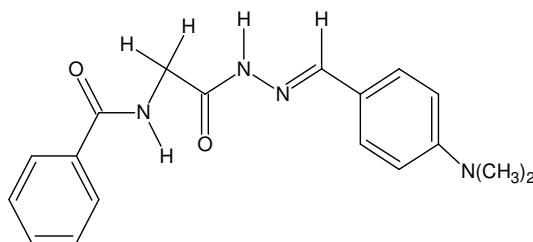
1: Structure of the ligand (HL)

EXPERIMENTAL

N-Benzoyl glycine purchased from E-merck was used as such for the preparation of the hydrazine derivative. The surfactants used in this study (Triton-X-100 and Labs.) were obtained from Sigma-Aldrich, USA and the metal chlorides were purchased from SRL, India. All the other chemicals used in this study were of AnalaR grade.

Potentiometric titrations were carried out on a pH Meter Systronic, μ-362 with a glass Calomel electrode assembly (± 0.01) which was connected to a thermostat of circular D_8-G Haake Mess Techinik. IR Spectra were obtained using a Shimadzu FTIR 8400 while the electronic spectra were taken on a Shimadzu 2450 UV-vis spectrophotometer. C, H and N were microanalyzed using a Perkin-Elmer model 240 ºC. Conductance of the complexes was measured on a Systronic Conductivity-meter 306. NMR Spectra were recorded on a Jeol AL 300 FT NMR spectrometer and mass spectra, from a Jeol Sx102/Da-6000 mass spectrometer. Magnetic susceptibility measurements were carried out on a magnetic susceptibility balance, Sherwood Scientific Cambridge, UK while the variable temperature magnetic susceptibility was measured using SQUID. RT and LNT ESR spectra of Cu(II) complex were obtained on a Varian E-line X band ESR spectrometer, using DPPH as a g-marker.

Preparation and analysis of the ligand: N-Benzoyl glycine hydrazide was prepared as reported[17]. 4-Dimethylamino benzylidene (N-benzoyl)glycyl hydrazone, HL was prepared by refluxing ethanolic solutions of N-benzoyl glycine hydrazide (1 g, 5 mmol) and 4-dimethylamino benzaldehyde (0.77 g, 7 mmol) for 4 h. The yellowish brown precipitate obtained on slow cooling of the reaction mixture was filtered, washed repeatedly with ethanol, recrystallized from hot ethanol and dried at room temperature. The compound thus obtained was characterized based on elemental, IR, ^{1}H and ^{13}C NMR and mass spectral data. Yield 60 %. m.p. 210-213 °C. M[+] peak at m/e 325 as the base peak in the mass spectrum of the ligand (Fig. 1).
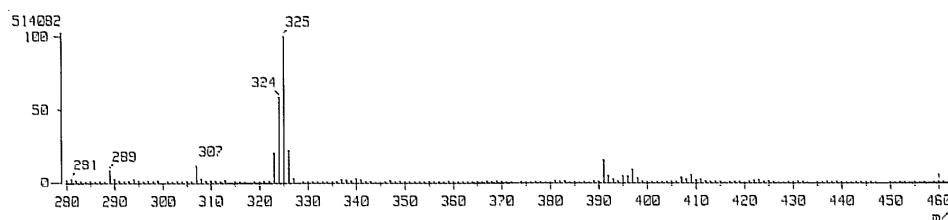

Fig. 1. Mass spectrum of HL

Preparation and analysis of the complexes: The complexes were prepared by refluxing the ethanolic solutions of 3 mmol HL (1 g of HL in 20 mL ethanol) with 3 mmol of the appropriate metal chloride. Formation of the Cu(II) complex started after refluxing the reaction mixture for 4 h and the red Cu(II) complex separated out on cooling was filtered, washed with ethanol and dried in air. However, Ni(II) and Cd(II) complexes could only be isolated after refluxing the solution for *ca.* 20 h and by adding *ca.* 20 mL of acetonitrile and THF to the concentrated reaction solutions. The precipitate so obtained were filtered, washed with acetonitrile and THF mixture and dried in desiccator. The metal ions and chlorine content were estimated following standard procedures[18]. Hydrazine was determined volumetrically by titrating against KIO_3 after subjecting the complex to acid hydrolysis. C, H and N were microanalyzed.

Preparation of the solutions for the potentiometric titrations: All the solutions used in the potentiometric titrations were prepared in double distilled water. The ligand solution prepared in 30 % aqueous-dioxane medium was used for the titration in aqueous medium. Critical micellar concentration's of Tx-100 and Labs. are 0.24 and 1.60 mmol, respectively. The solutions of the surfactants (5 mmol) well above their critical micellar concentrations were used for making the ligand solution for the potentiometric titrations. The metal-ligand molar ratio was kept constant at 1:2 in all media and the ionic strength of all the reaction mixtures was maintained at 0.1 M by using 0.5 M KNO_3 as a background electrolyte. The titrations were performed over the pH range 2.5-12.0 with standard KOH solution and all the titrations were thermostated at the desired temperature.

RESULTS AND DISCUSSION

The analytical data (Table-1) shows that HL reacts with Ni(II), Cu(II) and Cd(II) chlorides in ethanolic medium yielding addition complexes of 1:1 metal-ligand stoichiometries. All the complexes are stable under ordinary conditions. Cu(II) and Ni(II) complexes decompose at 230 and 220 °C, respectively while Cd(II) complex is non-melting till 250 °C. The complexes are insoluble in common organic solvents. They are soluble only in DMSO and DMF. Thermal studies in the 120-160 °C temperature range correspond to the presence of one coordinated water molecule in the Ni(II) and Cd(II) complexes. Molar conductance values in 0.001 M DMF solution show that Cu(II) complex is non electrolyte while Ni(II) and Cd(II) complexes behave as 1:1 electrolytes[19].

TABLE-1
ANALYTICAL DATA, YIELD (%), COLOUR AND MOLAR CONDUCTANCE
(Ω^{-1} cm^2 mol^{-1}) DATA OF THE LIGAND (HL) AND ITS METAL COMPLEXES

Complex (Colour)	Yield (%)	m.p. (°C)	Found (calcd) (%)						Molar conductance
			M	Cl	C	H	N	N_2H_4	
HL (Brown)	70	213	–	–	66.96 (66.60)	6.20 (6.17)	16.97 (17.28)	9.90 (9.80)	–
[Ni(HL)(H$_2$O)Cl]Cl (Green)	60	220^d	12.70 (12.44)	15.00 (15.05)	45.43 (45.79)	4.25 (4.66)	11.63 (11.87)	6.83 (6.78)	62
[Cu(HL)(OH)$_2$] (Red)	50	230^d	15.21 (15.07)	–	50.89 (51.24)	5.32 (5.22)	13.20 (13.28)	–	–
[Cd(HL)(H$_2$O)Cl]Cl (Red)	70	>250	20.80 (21.39)	13.42 (13.51)	41.02 (41.11)	4.12 (4.19)	10.42 (10.66)	5.68 (6.09)	61

d: Decomposition temperature.

Potentiometric studies: The potentiometric titrations of HL and the Cu(II), Ni(II) and Cd(II) complexes in aqueous and aqueous-micellar media at ionic strength 0.1 M KNO$_3$ were carried out against standard 0.05 M KOH at 17, 27 and 37 °C and Fig. 2 exhibits the potentiometric titration curves at 27 °C where curve (a) represents the acid curve in aqueous medium, curve (b) the ligand curve in aqueous medium and curves (c-k), the metal-ligand curves for Ni(II), Cu(II) and Cd(II) complexes in aqueous and aqueous-micellar media. The ligand curve shows a single inflection in the 4-11 pH ranges in all the media at all the temperatures corresponding to the neutralization of only one proton. Addition of metal ion to the free ligand solution shifts the buffer region of the ligand to a lower pH value as observed in the curves (c-k). This shows that complex formation proceeds by releasing proton from the base. Similar curves are obtained for the titrations of M(II)-HL complexes at 17 and 37 °C. The proton-ligand and metal-ligand formation curves at different tempe-ratures in aqueous and aqueous-micellar media are obtained from the pH-metric titration data employing Irving and Rossotti's pH-metric titration technique[20,21]. Fig. 3 shows the proton-ligand formation curves in different media at 27 °C where

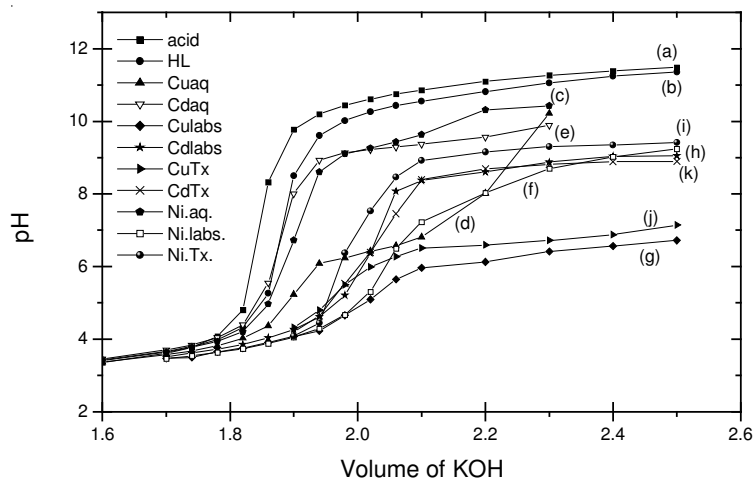Fig. 2.   Potentiometric titration curves of HL and the Cu(II), Ni(II) and Cd(II) complexes at 27 ℃ and 0.1 M ionic strength in different media

the curves extend from 0.40-0.95 on the $\bar{n}_H$ scale indicating dissociation of only one proton from HL. In the formation curves of Ni(II), Cu(II) and Cd(II) complexes in aqueous and aqueous-micellar media at 27 °C (Fig. 4), the value of $\bar{n}$, $0.1 < \bar{n} > 0.96$ in all the media suggests that HL forms only 1:1 complexes with the metal ions. The protonation constant of HL, log K_1^H and metal-ligand stability constant, log K^{ML} for the formation of Ni(II), Cu(II) and Cd(II) complexes were evaluated from the formation curves using Bjerrum's half integral method[22]. The values so obtained in aqueous and aqueous-micellar media at different temperatures are collected in
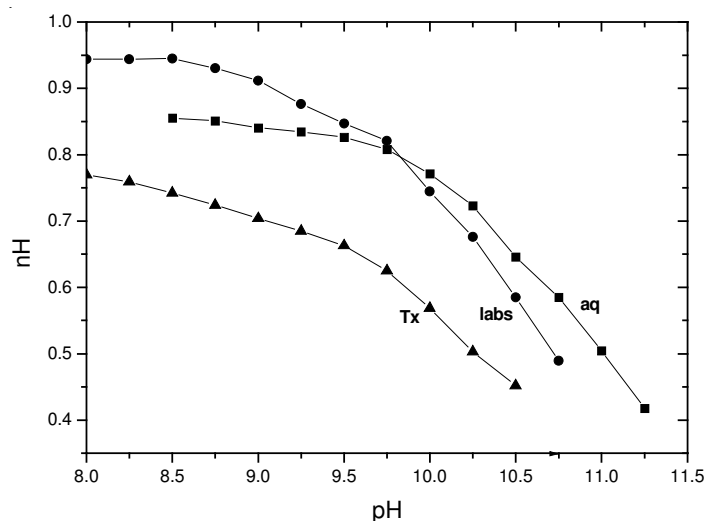

Fig. 3.   Protonation curves of HL in different media at 27 °C. $\bar{n}_H$ is the average number of protons associated with the ligand
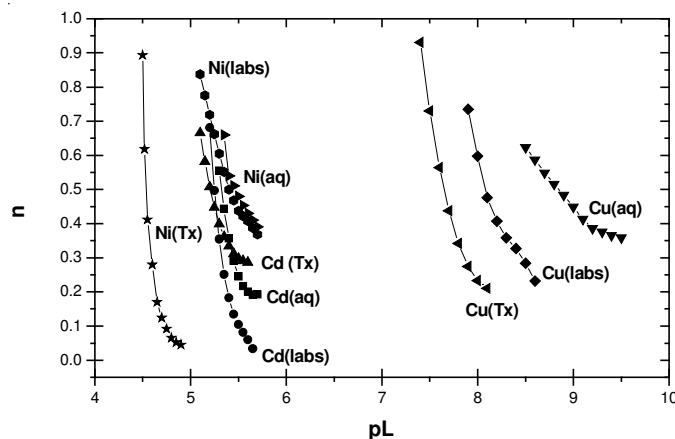
Fig. 4.   Metal-ligand formation curves in different media at 27 °C. $\bar{n}$ is the number of ligands attached per metal ion and pL is the free ligand exponent

Table-2. The values of log K_1^H and log K^{ML} are found to decrease with increase in temperature indicating that both protonation and complex formation are more favourable at low temperature. This behaviour may be mainly ascribed to the thermal hydrolysis of the metal complexes[22]. The stability of the complexes falls in the Irving-Williams order[23]: Cu(II) > Ni(II) > Cd(II). The higher values of log K^{ML} in the case of Cu(II) chelates are due to Jahn-Teller effect.

A significant variation in the magnitudes of protonation constant of the ligand and the formation constants of the Ni(II), Cu(II) and Cd(II) complexes in aqueous-micellar media compared to the aqueous solution and in the pattern of the formation curves of the complexes in different media is observed in the figures. There is also a systematic and significant decrease in the log K_1^H and log K_{ML} values in the order: aq. > Labs > Tx-100. It shows that protonation of the ligand and the formation of the complexes are more favourable in aqueous media and inhibited by the presence of surfactants in the reaction media. It has been interpreted by considering the partitioning of the reactants between the micellar and aqueous phase[24,25]. There is an increased partitioning of the ligand in favour of the micellar pseudophase and if the actual complexation reaction is assumed to take place in the bulk aqueous phase, the stability constant falls. The decrease in the stability of the complexes in micellar media suggests that the ligand molecules with large hydrophobic groups are preferably drawn into the hydrophobic core of the micelles while the metal ions are dispersed between the Stern layer and the bulk solution. This limits the ligands available to the metal ions because only the metal ions in the vicinity of the Stern layer can interact with the ligands. Hence, the possibility to form complexes decreases in micellar media thereby resulting in the decrease in the stability constant values. Further, decrease in the dielectric constant of the media due to the presence of the surfactants destabilizes the charged complex species thereby decreasing the log K^{ML} values.

TABLE-2
STABILITY CONSTANTS AND THERMODYNAMIC PARAMETERS OF THE LIGAND
(HL) AND ITS METAL COMPLEXES AT 0.1 M IONIC STRENGTH (KNO₃) AND AT
DIFFERENT TEMPERATURES IN AQUEOUS AND AQUEOUS MICELLAR MEDIA

Media	Temperature (°C)	Parameters	Metal ions			
			H⁺	Ni	Cu	Cd
Aq	17	log K^{ML}	11.18[a]	5.89	9.09	5.78
		-ΔG[b]	14.83	7.81	12.06	7.67
	27	log K^{ML}	11.01[a]	5.47	8.85	5.33
		-ΔG[b]	15.11	7.50	12.15	7.30
		-ΔH[b]	9.58	11.28	26.38	9.43
		-ΔS[c]	18.43[d]	13.62	47.40	7.08
	37	log K^{ML}	10.71[a]	5.34	7.79	5.19
		-ΔG[b]	15.19	7.57	11.05	7.35
Labs	17	log K^{ML}	10.83[a]	5.74	8.28	5.64
		-ΔG[b]	14.37	7.62	10.99	7.48
	27	log K^{ML}	10.72[a]	5.40	8.08	5.25
		-ΔG[b]	14.72	7.41	11.09	7.21
		-ΔH[b]	5.57	11.29	14.61	11.15
		-ΔS[c]	30.50[d]	12.93	12.90	13.14
	37	log K^{ML}	10.56[a]	5.20	7.57	5.11
		-ΔG[b]	14.98	7.57	10.74	10.74
Tx-100	17	log K^{ML}	10.92[a]	5.35	8.78	5.37
		-ΔG[b]	14.49	7.10	11.65	7.13
	27	log K^{ML}	10.27[a]	4.54	7.65	5.20
		-ΔG[b]	14.10	6.23	10.50	7.14
		-ΔH[b]	20.00	18.92	29.58	12.68
		-ΔS[c]	19.67	42.30	63.59	18.48
	37	log K^{ML}	9.96[a]	4.46	7.38	4.75
		-ΔG[b]	14.14	6.33	10.47	6.74

a: Protonation constant (log K_1^H) of HL. b: ΔG and ΔH in kcalmol⁻¹. c: ΔS in cals/deg/mol. d: ΔS is positive.

Anionic Labs micelles have negatively charged Stern layer which can attract the positively charged species, stabilizing it on the surface of the micelles. This will bring the positively charged metal ions closer to the ligands trapped in the core of the micelles. Nonionic surfactants Tx-100 micelles have neutral surface and cannot stabilize the charged species on its surface. Thus, the formation of the complexes is more favoured in Labs micelles than in Tx-100 medium as observed.

Thermodynamic parameters of the complexation reactions: The overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) associated with both the protonation and complexation reactions in aqueous and micellar media are included in Table-2. Negative ΔG values for the reactions indicate spontaneity of the reactions in all the media. For the protonation of HL, negative ΔH and positive ΔS values in aqueous and Labs media show that formation of L⁻ is both enthalpy- and

entropy-driven process. However, in Tx-100, heat of reaction for the protonation is comparatively high and ΔS value is negative. Negative ΔG and ΔH indicate the spontaneity and exothermic nature of all the complexation reactions. Table-2 shows that the ΔG values have no sharp behaviour with temperature and the thermodynamic parameters are perturbed by the presence of micelles in the reacting systems. ΔG values for the complexation reactions are the highest in the aqueous medium while ΔH and ΔS values are the highest in Tx-100 medium. This observation shows that complexation is favoured most in aqueous media as compared to the micellar media. Negative ΔS values indicate that the complexes are highly solvated.

Magnetic moment and electronic spectral studies: The red Cu(II) complex is paramagnetic with μ_{eff} value 2.14 BM corresponding to the presence of one unpaired electron. The susceptibility of the Cu(II) complex *versus* temperature is presented in Fig. 5. In both FC and ZFC modes, the magnetization values are almost the same in the temperature range 5-300 K (-268-27 ℃) indicating paramagnetic behaviour[26]. The spin dependence is high below 50 K (-223 ℃) following Curie's law while it is low above 50 K upto 300 K (27 ℃) obeying Pauli paramagnetism. The electronic spectrum of the Cu(II) complex shows a broad band at 520 nm with a shoulder at 400 nm assignable to the transitions $^2B_{1g} \rightarrow {}^2B_{2g}(D)$ and $^2B_{1g} \rightarrow {}^2A_{1g}(D)$, respectively of a square planar geometry around the metal ion[27]. A band at 320 nm observed in the electronic spectrum of the complex is attributable to the Cu(II)-OH charge transfer band[28]. The μ_{eff} value (3.78 BM) and a strong band at the 667 nm with weak shoulders at 720 and 550 nm in the electronic absorption spectrum of the Ni(II) complex which may be assigned to the $^3T_1(F) \rightarrow {}^3T_1(P)$ transition, suggest a tetrahedral geometry around Ni^{2+} ion[27].
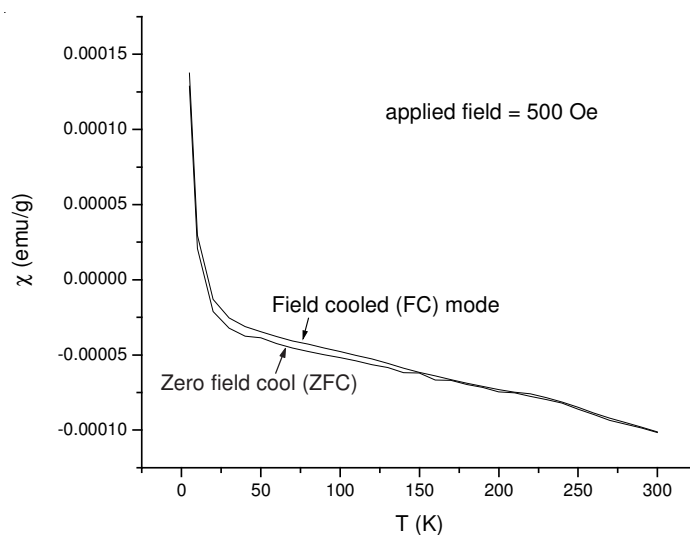

Fig. 5. Magnetic susceptibility of [Cu(HL)(OH)$_2$] as a function of temperature. T is in absolute scale

ESR Spectra: The room and liquid nitrogen temperature ESR spectra of Cu(II) complex are isotropic in nature and show only one intense band each. The g-values at RT (2.088) and LNT (1.988) are very close to the reported g-values of square planar Cu(II) complexes (2.089)[28] and (2.06-2.10)[29,30] and much lower than expected for 'O$_h$' complexes 2.33931 indicating distortion of the Cu(II) complex to square planar coordination.

Infrared spectra: The bonding sites of HL have been assigned by a careful comparison of IR spectra of the complexes with that of the ligand. Broad bands at *ca.* 3350 cm^{-1} observed in the spectra of Ni(II) and Cd(II) complexes are due to ν(OH)[31,32]. The IR spectrum of HL shows bands at 1676, 1554 and 1371 and 1637, 1529 and 1313 cm^{-1} which may be assigned to amide I, II and III modes of the hydrazidic and benzamide moieties, respectively. The amide bands of the benzamide group remain almost unaltered in the spectra of the complexes showing non-involvement of the group in bonding. However, the corresponding amide bands of the hydrazidic moiety show bathochromic shift for the amide I (5-31 cm^{-1}) and II bands (8-31 cm^{-1}) and hypsochromic shift (5-40 cm^{-1}) for the amide III bands in the spectra of the complexes indicating participation of the hydrazidic >CO in complexation. Coordination through the azomethine nitrogen[33] has been inferred from the observed bathochromic shift (14-41 cm^{-1}) in ν(C-N) and hypsochromic shift (12-14 cm^{-1}) in the ν(N-N) bands in the spectra of the complexes. The bands appearing in the 443-435 cm^{-1} region in the spectra of the complexes are assigned to the ν(M-O) modes, showing that the carbonyl oxygens have formed coordinate bonds with the metal ions.

Elemental analysis data shows that chlorine is absent in the Cu(II) complex. Magnetic susceptibility studies indicate the complex to be paramagnetic with one unpaired electrons. Thus, the charge balance of the molecular formula for the complex requires that water molecules deprotonate and participate in the complex formation as hydroxide ions. Similar type of bonding is reported for Zn(II) complex[34]. Since no broad band characteristic of water molecule(s) is observed at 3300 cm^{-1} in the IR spectrum of Cu(II) complex, presence of water molecules in the complex is excluded. However, appearance of a new band at 1076 cm^{-1} in the spectrum of the complex, attributable to the MOH bending, suggests formation of Cu-OH bond[32]. A strong band observed at 320 nm in the electronic spectrum of Cu(II) complex also supports the formation of Cu-OH.

^{1}H and ^{13}C NMR spectra: In the ^{1}H NMR spectrum of HL, the singlet at δ 11.03 and the triplets at δ 8.66 and 8.47 have been assigned to -NN<u>H</u>CO and C$_6$H$_5$CON<u>H</u>- protons. The singlet at δ 7.90 and doublets at δ 4.24 and 3.80 are, respectively assigned to -NC<u>H</u> proton and -CH$_2$ protons. Nine ring protons resonate as multiplets at δ 7.25-7.74 while the singlet at δ 2.70 showing an integration of 3H is assigned to CH$_3$ protons. In the ^{1}H NMR spectrum of [Cd(HL)Cl(H$_2$O)]Cl, the signal due to -N-N<u>H</u>CO shows a downfield shift (δ, 0.18), suggesting participation of the hydrazidic >CO and azomethine nitrogen in bonding[35].

The ^{13}C NMR spectrum of HL shows a singlet at 170.63 ppm due to carbonyl carbon of the -NNH<u>C</u>O moiety and a doublet at 167.48 ppm assignable to the carbonyl carbon of the C$_6$H$_5$CONH- group. The singlets at 40.07 and 42.88 ppm are, respectively assigned to the -CH$_3$ and -CH$_2$ carbons. The ring carbons resonate as singlets at 112.63-152.31 ppm. In the ^{13}C NMR spectrum of [Cd(HL)Cl(H$_2$O)]Cl, the singlet due to -NNH<u>C</u>O carbon shows a shift (0.93 ppm) showing that the hydrazidic carbonyl participates in complexation. However, the other ^{13}C signals do not show any significant shift in the spectrum of the complex.

Presence of only one dissociable proton in the ligand is shown by the potentiometric studies in aqueous and aqueous-micellar media. Since hydrazones are reported[2-4] to form bonds to the metal ions through carboxylic oxygen and hydrazinic nitrogen/nitrogen of the imino-group in aqueous medium where there is a conjugate chelate ring formed by ligand enolization in the complexes, HL is also expected to exhibit keto-enol tautomerism and the amido proton can be dissociated through enolization as shown in (1).

R = C$_6$H$_5$C(O)NHCH$_2$-

Keto form   Enol form   (I)
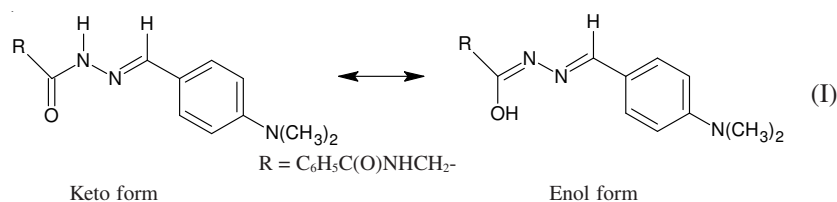
Thus, in aqueous and aqueous-micellar media, HL acts as a uninegative species. However, in ethanolic medium, HL acts as a neutral species forming adducts. Formation curves of the complexes indicate formation of only 1:1 metal-ligand complexes. Based on the foregoing discussions, tetracoordination of the metal ions is suggested where HL binds to the metal ions as a bidentate ligand coordinating through the hydrazidic carbonyl oxygen and azomethine nitrogen. Tetrahedral geometry for [NiCl(HL)(H$_2$O)]Cl and [Cd(HL)Cl(H$_2$O)]Cl complexes and square planar geometry for [Cu(HL)(OH)$_2$] complex are tentatively proposed (Fig. 6).
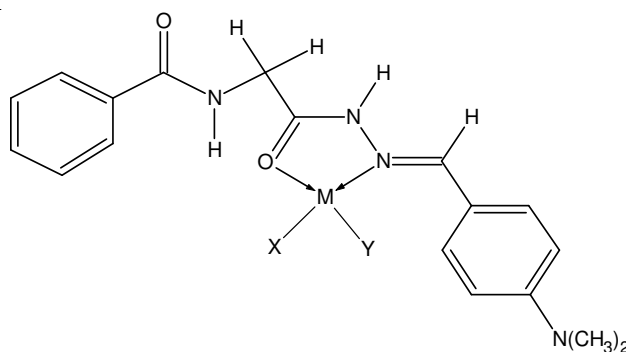
Fig. 6.   Tentative structure proposed for the complexes (M = Ni and Cd, X = Cl, Y = H$_2$O; M = Cu, X = Y = OH

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