Stereochemistry of New Nitrogen Containing Heterocyclic Aldehyde. VII. Potentiometric, Conductometric and Thermodynamic Studies of Novel Quinoline Azodyes and Their Metal Complexes with Some Transition Metals

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A novel series of quinoline azodyes (5-(4′-derivatives phenyldiazo)-8-hydroxy-7-quinolinecarboxaldehyde)) (HL_1—HL_5) has been prepared and characterized by elemental analyses, ^{1}H-NMR and IR spectra. The IR spectral data indicate that the compounds can exist in two resonance structures. Proton–ligand dissociation constants of quinoline azodyes and their subsituted derivatives, and metal–ligand stability constants of their complexes with bivalent (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) metal ions have been determined potentiometrically in 0.1 M KCl and 40% (v/v) dimethylformamide (DMF)–water mixture. The influence of substituents on the dissociation and stability constants was examined on the basis of the electron repelling property of the substituent. The order of the stability constants of the formed complexes was found to be $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$. The effect of temperature was studied and the corresponding thermodynamic parameters (ΔG, ΔH, ΔS) were derived and discussed. The stoichiometries of these complexes were determined conductometrically and indicated the formation of 1:1 and 1:2 (metal:ligand) complexes was indicated.

Key words quinoline azodye; potentiometry; conductometry; complexation; thermodynamic

El-Sonbati and El-Bindary focussed their research on the insertion reaction involving monomeric and polymeric model complexes of quinoline azodyes.[1,2]

As part of our studies on simple inorganic models of interest for the development of the bioinorganic chemistry of uranium,[2] we have started investigation on a dioxouranium(VI) complex with 8-hydroxyquinoline azodye derivatives which appear to be suitable models due to the pretence of dioxouranium(VI) for oxygen donors in biological systems. The chemistry of quinoline and its derivatives has attracted special interest due to their therapeatic properties.[3] Quinoline sulphonamides have been used in treatment of cancer,[4] turberculosis,[5] and malaria.[6]

Azo compounds based on quinoline play a central role as chelating agents for a large number of metal ions, as they form a stable six-membered ring after complexation with the metal ion and can also be used as analytical reagents.[7] Dimethylformamide (DMF) or DMF/water mixtures as solvent can be used due to: i) hydrolytic reactions of highly charged metal ions; ii) insolubility of the ligand or of one or more of the complexes to be formed. DMF is an aprotic solvent which readily dissolves many water-soluble salts as well as other sparingly soluble substances.[8]

In continuation of our earlier work,[9,10] we report herein the synthesis of quinoline azodyes (Chart 1) and the stability constants of Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} complexes with quinoline azodyes at different temperatures. Ionization potential and substituent effects on the dissociation and stability constants are also investigated. Furthermore, the corresponding thermodynamic functions of complexation are evaluated and discussed. Moreover, the stoichiometries of these complexes are determined conductometrically at 298 K.

Experimental

Preparation of the Ligands 8-Hydroxy-7-quinolinecarboxaldehyde was prepared according to El-Sonbati and El-Bindary.[11] The standard chem-

ical aniline and 4-alkyl-anilines (alkyl: CH_3, OCH_3, Cl, NO_2; Aldrich Chemical Co.) were used without any further purification. The experimental technique has been described previously.[1,2,11]

The novel 5-(4′-derivatives phenyldiazo)-8-hydroxy-7-quinolinecarboxaldehyde) (HL_n) were prepared from aniline or its *p*-substituted derivatives (10 mmol) was dissolved in hydrochloric acid (20 mmol/25 ml distilled H_2O). The hydrochloric compound was diazotized below −5 °C with a solution of sodium nitrite (0.8 g, 10 mmol, 30 ml distilled H_2O). The diazonium chloride was coupled with an alkaline solution of oxine (1.7 g, 10 mmol) in 20 ml of ethanol. The crude dye was collected by filtration and was crystallized from DMF, then dried in a vacuum dessicator over P_2O_5.

Reagents and Materials Metal ion solutions (0.0001 M) were prepared from Analar metal chlorides in bidistilled water and standardized with EDTA.[12] The ligand solutions (0.001 M) were prepared by dissolving the accurate weight of the solid in DMF (Analar). Solutions of 0.001 M HCl and 1 M KCl were also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 40% (v/v) DMF–water mixture was used as titrant and standardized against oxalic acid (Analar).

Potentiometric Measurements The apparatus, general conditions and methods of calculation were the same as in the previous work.[9,10] The following mixtures were prepared and titrated potentiometrically at 298 K against standard 0.004 M NaOH in 40% (v/v) DMF–water mixture:

i) 5 ml 0.001 M HCl+5 ml 1 M KCl+20 ml DMF;
ii) 5 ml 0.001 M HCl+5 ml 1 M KCl+15 ml DMF+5 ml 0.001 M ligand;
iii) 5 ml 0.001 M HCl+5 ml 1 M KCl+15 ml DMF+5 ml 0.001 M ligand+5 ml 0.0001 M metal chloride.

For each mixture, the volume was made up to 50 ml with bidistilled water before the titration. These titrations were repeated for temperatures of 308 and 318 K. A constant temperature was maintained at ±0.05 K by using an ultrathermostat (Neslab 2 RTE 220). The pH-meter readings in 40% (v/v) DMF–water mixture are corrected according to the Van Uitert and Hass relation.[13]

Conductometric Measurements Solutions of 10^{-4} M of metal chloride were titrated with 10^{-3} M of ligands. These titrations were performed using YSI model 32 conductance-meter and carried out at 298 K.

Results and Discussion

Characterization of the Azo Compounds Analytical data (Table 1) are in agreement with the proposed formulae.

The ^{1}H-NMR spectra show that the ligands exist as a broad signal due to C_8-OH. This favours formation of an in-

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tramolecular hydrogen bond with the CO group. Electron-withdrawing substituents reduce considerably the intramolecular hydrogen bond as indicated by the marked shift of the hydroxyl signal to a higher field in the p-NO$_2$ and p-Cl compounds. Electron-donating substituents give the opposite effect, arising from the increasing basicity of the azo-nitrogen.

The electronic absorption spectra of the ligands exhibit mainly five bands (A—D, F). The band A located at 41666—35710 cm^{-1} could be assigned to the low energy $\pi-\pi^*$ transition corresponding to the aromatic system. The band B within 32260—29410 cm^{-1}; can be assigned to the $\pi-\pi^*$ transition of the CO group. The band C appearing within

Table 1.   Analytical Data of Quinoline Azodyes[a]

Compound[b]	Exp. (Calcd) %		
	C	H	N
HL$_1$	66.6 (66.5)	4.2 (4.2)	13.5 (13.7)
HL$_2$	70.0 (70.1)	4.6 (4.5)	14.6 (14.4)
HL$_3$	69.4 (69.3)	3.9 (4.0)	15.0 (15.2)
HL$_4$	61.5 (61.6)	3.2 (3.2)	13.3 (13.5)
HL$_5$	59.7 (59.6)	3.0 (3.1)	17.5 (17.4)

a) Further studies with title ligands, using different metal ions, are in progress and will be published in due coarse.   b) The analytical data agree satisfactory with the expected formulae represented as given in Chart 1 (see Experimental). HL$_1$—HL$_5$ are the ligand as given in Chart 1. Air-stable, high melting temperature, coloured. Insoluble in water, but partially soluble in hot ethanol, and soluble in coordinating solvent. Decomposition near 275 °C. Around 350 °C the decomposition showed for a short period and became rapid again at about 430 °C. The ligands were completely decomposed at 590 °C.

26310—24390 cm^{-1}, can be is assigned to $\pi-\pi^*$ transition within the C=N group. The band D within 24390—23800 cm^{-1} assigned to the $\pi-\pi^*$ transition of the azo-form. The band F located at 21740—20400 cm^{-1}. These latter bands can be assigned to intramolecular charge transfer interactions within the whole molecule (CT).

By tracing the IR spectra of the azo compounds, no νNH$_2$ stretching vibrations are apparent. This supports the formation of azodye ligands. The mode of bonding of the HL$_n$ to the metal ions was elucidated by investigating the IR spectra of the complexes on the basis of a comparative analysis of the results with respect to literature data of related systems. The positions of the most relevent and characteristic bands are due to: i) carbonyl oxygen atom, ii) azo nitrogen, iii) OH group and iv) CN$_{Py}$ group.

The spectra exhibit a medium to strong band in the region 1400—1500 cm^{-1} which could be assigned to $\nu_{N=N}$ stretching vibration.[1,2] The $\nu_{C=C}$ stretching vibrations of the phenyl ring are traced at 1500—1600 cm^{-1} which are due to the symmetric and assymetric vibrations, respectively. The investigation of Rossmey and Mecke[14] on deuterated phenolic derivatives showed that the higher frequency band would be related to δ OH, whereas the band within 1100 cm^{-1} can be due to ν_{C-OH}. The higher value of the δ OH may account for the existence of hydrogen bonding. Califan and Luttke[15] found that the –OH in hydroxy compounds suffered a blue shift when the OH group is involved in a hydrogen bond.

Much has been written about the –OH stretching frequency and intensity of phenol derivatives depending on many factors (e.g. substituent, medium, ... etc.). The study of IR frequencies is especially useful in the analysis of the properties of hydrogen bonds.

On turning our attention to the IR spectra of hydrogen

n = 1   R= -OCH$_3$
n = 2   R= -CH$_3$
n = 3   R= -H
n = 4   R= -Cl
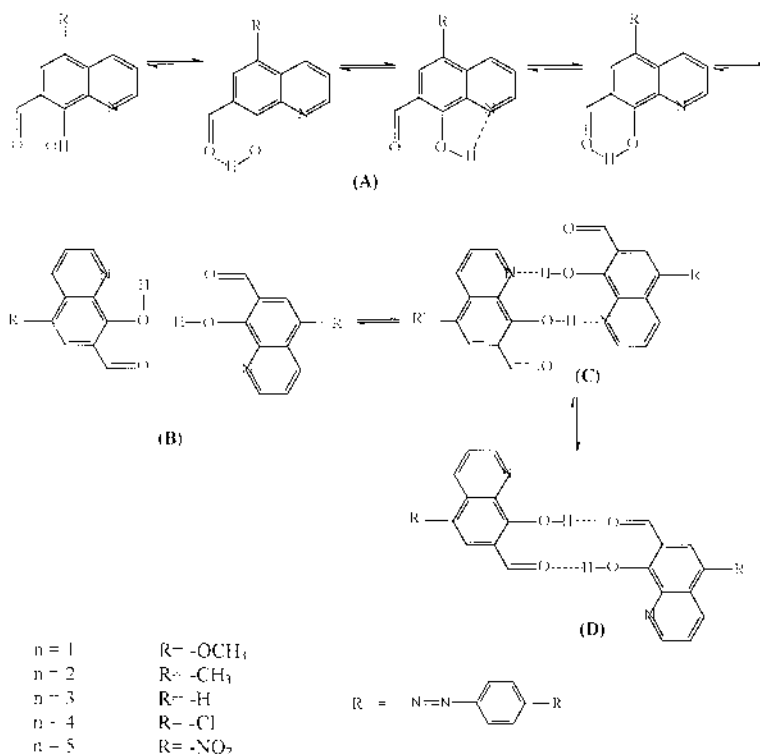n = 5   R= -NO$_2$

R = N=N—〈 〉—R

Chart 1.   General Formula and Proton Numbering Scheme of the HL$_n$

containing azo compounds such as HL_n (Chart 1), the $\nu_{N=N}$ showed a series of medium to weak bands at 1430, 1490 and 1520 cm^{-1}. These besides the very broad bands centered at *ca.* 3500 and *ca.* 2900 cm^{-1} may exist on a six membered chelate skeleton. The hydrogen bonding in this compounds could be classified into types according to the position of the –OH group, vis. i) intramolecular hydrogen bonding between the C_8-OH and CO and/or CN (Chart 1A) and ii) intermolecular hydrogen bonding resulting from the C_8-OH group through two molecules (Chart 1B) and/or C_8-OH with CN (Chart 1C) or CO (Chart 1D) through two molecules. This could be confirmed by the appearance of the high frequency band (*ca.* 3500 cm^{-1}) as a result of intermolecular hydrogen bonding and that at lower frequency (*ca.* 2900 cm^{-1}) due to the intramolecular hydrogen bonding.

Coggeshall,[16] Diab and El-Sonbati[17] found three kinds of bonded-OH structures on the basis of the frequencies: i) only the oxygen is in the bridge while the hydrogen is free, ii) a polymer chain is formed in which both hydrogen and oxygen atoms participate in the hydrogen bond, iii) dimer associates are formed.

The IR spectral data of HL_n exhibits a weak band at *ca.* 1655 cm^{-1}. This is a criterion for $\nu_{C=O}$ of the aldehydic group. A very strong band at 1585±10 cm^{-1} is apparent and assignable to $\nu_{C=C}$ of the phenyl ring. The very interesting region is that in the frequency range 2800—3550 cm^{-1}. This is a characteristic region to the vibrational frequency of the –OH group where vibrational bands at 2900 cm^{-1} of medium appearance and a broad at 3400—3550 cm^{-1} are apparent. This is a powerful finding which indicates two types of hydrogen bonding: i) intramolecular one between –OH and aldehydic group (Chart 1A), ii) intermolecular one between –OH and aldehydic group through two molecules (Chart 1D).

In our laboratory, El-Sonbati and El-Bindary[1,2,17—20] published a series of papers to spotlight the chemistry, structural models and chemical equilibria of azo compounds and their complexes. The presentations and discussions explored many important points and still many questions remain.

Potentiometric Studies. Proton–Ligand Stability Constants The average number of protons associated with the ligands at different pH values, $\bar{n}_A$, were calculated from the titration curves of the acid in the absence and presence of a ligand. Thus, the formation curves ($\bar{n}_A$ *vs.* pH) for the proton–ligand systems were constructed and found to extend between 0 and 1 in the $\bar{n}_A$ scale. This means that ligands have one ionizable proton (the enolized hydrogen ion of the hydroxyl group in the quinoline moiety). It can be seen that for the same volume of NaOH added the ligand titration curves had a lower pH value than the acid titration curve. The displacement of a ligand titration curve along the volume axis with respect to the acid titration curve is an indication of proton dissociation. The proton–ligand stability constants were calculated using the method of Irving and Rossotti.[21]

The phenolic –OH group is known to be weakly acidic, indicating a stronger bonding between the proton and the oxygen donor. This means that the proton–ligand stability constant of quinoline azodyes should be high due to the dissociation of the –OH group.[22]

Substituent Effect on pK An inspection of the results in Table 2 reveals that the pK^H values of HL_3 and its substituted

Table 2. Thermodynamic Functions for the Dissociation of Quinoline Azodyes in 40% (v/v) DMF–Water Mixture and 0.1 M KCl at Different Temperatures

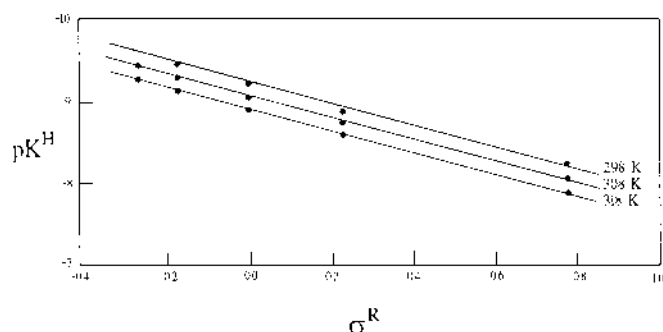| Compound	Temp. (K)	Dissociation constant pK^H	Free energy change (kJ mol^{-1}) ΔG	Enthalpy change (kJ mol^{-1}) ΔH	Entropy change (J mol^{-1} K^{-1}) $-\Delta S$
HL_1	298	9.62	54.89		132.18
	308	9.45	55.72	15.50	130.58
	318	9.27	56.44		128.74
HL_2	298	9.45	53.92		141.10
	308	9.30	54.84	11.87	139.51
	318	9.13	55.59		137.48
HL_3	298	9.21	52.55		135.23
	308	9.05	53.37	12.25	133.50
	318	8.89	54.12		131.66
HL_4	298	8.85	50.49		133.45
	308	8.72	51.42	10.72	132.14
	318	8.55	52.05		129.96
HL_5	298	8.20	46.78		102.38
	308	8.01	47.23	16.27	100.50
	318	7.83	47.87		99.37

Fig. 1. Correlation of pK^H with the Hammett's Constant σ^R at 298, 308 and 318 K

derivatives are influenced by the inductive or mesomeric effect of the substituents. The p-OCH$_3$ and p-CH$_3$ derivatives (HL_1, HL_2) have a lower acidic character (higher pK^H values) than the p-Cl and p-NO$_2$ derivatives (HL_4, HL_5). This is quite reasonable because the presence of p-OCH$_3$ and p-CH$_3$ groups (*i.e.* an electron donating effect) will enhance the electron density by their high positive inductive or mesomeric effect, whereby a stronger O–H bond is formed. The presence of p-Cl and p-NO$_2$ groups (*i.e.* an electron withdrawing effect) will lead to the opposite effect.

The results are also in accordance with Hammett's *para* substituent constant values σ^R.[23] Straight lines are obtained on plotting pK^H values at different temperatures *versus* σ^R (Fig. 1). The *para* substituents in the quinoline moiety have a direct influence on the pK^H values of the investigated compounds, revealing the coplanarity of the molecule and thus affording a maximum resonance *via* delocalization of its π-system.

Metal–Ligand Stability Constants The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ions ($\bar{n}$) *versus* the free ligand exponent (pL), according to Irving and Rossotti.[24] These curves were analyzed and the successive

Table 3. Stepwise Stability Constants for the Complexation of Substituted Quinoline Azodyes with Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} in 40% (v/v) DMF–Water Mixture and 0.1 M KCl at Different Temperatures

Compound	M^{n+}	298 K		308 K		318 K	
		$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
HL_1	Mn^{2+}	7.55	5.65	7.74	5.83	7.95	5.98
	Co^{2+}	7.70	5.73	7.88	5.90	7.99	6.05
	Ni^{2+}	7.75	5.77	7.93	5.96	8.08	6.12
	Cu^{2+}	7.90	5.99	8.10	6.12	8.25	6.28
HL_2	Mn^{2+}	7.35	5.47	7.59	5.64	7.80	5.82
	Co^{2+}	7.51	5.55	7.74	5.72	7.86	5.92
	Ni^{2+}	7.57	5.60	7.79	5.77	7.96	5.97
	Cu^{2+}	7.72	5.81	7.91	5.98	8.16	6.20
HL_3	Mn^{2+}	7.20	5.33	7.41	5.50	7.63	5.78
	Co^{2+}	7.34	5.41	7.54	5.57	7.80	5.85
	Ni^{2+}	7.41	5.48	7.52	5.65	7.85	5.94
	Cu^{2+}	7.60	5.70	7.70	5.86	7.99	6.15
HL_4	Mn^{2+}	6.81	4.95	7.18	5.26	7.42	5.53
	Co^{2+}	6.95	5.05	7.32	5.37	7.67	5.60
	Ni^{2+}	7.06	5.16	7.35	5.41	7.71	5.65
	Cu^{2+}	7.25	5.34	7.50	5.55	7.87	5.80
HL_5	Mn^{2+}	6.77	4.89	7.00	5.05	7.20	5.30
	Co^{2+}	6.85	4.95	7.09	5.10	7.30	5.36
	Ni^{2+}	6.99	5.06	7.25	5.18	7.44	5.45
	Cu^{2+}	7.20	5.20	7.43	5.31	7.63	5.60

stability constants were determined using different computational methods[25,26] which agree within 1% error. Accordingly the average values are represented in Table 3. The following general remarks can be pointed out:

i) The maximum value of $\bar{n}$ was ≈ 2 indicating the formation of 1:1 and 1:2 (metal:ligand) complexes only.

ii) The metal ion solution used in the present study was very dilute (10^{-4} M), hence there was no possibility of formation of polynuclear complexes.[27]

iii) The metal titration curves were displaced to the right-hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to ligand titration curves point to the formation of strong metal complexes.[28]

iv) In most cases, the colour of the solution after complex formation was observed to be different from the colour of the ligand at the same pH.

v) For the same ligand at constant temperature, the stability of the chelates increases in the order $Cu^{2+}>Ni^{2+}>Co^{2+}>Mn^{2+}$.[9,29] This order largely reflect the changes in heat of complex formation across the series from a combination of the influence of both the polarizing ability of the metal ion[30] and the crystal-field stabilization energies.[31] The greater stability of Cu^{2+} complexes is produced by the well known Jahn–Teller effect.

Effect of the Substituent R on the Stability of the Complexes An inspection of the results in Table 3 reveals that the stability constant values of the complexes of HL_3 and its substituted derivatives are influenced by the inductive or mesomeric effect of the substituents. This behaviour correlates with the effect of substitution on the phenyl ring as follows:

i) The high stability of HL_1 and HL_2 complexes can be attributed to the presence of the OCH_3 and CH_3 groups in the p-position relative to the azo group, respectively. This is

quite reasonable because the presence of p-OCH_3 and p-CH_3 groups (i.e. an electron donating effect) will enhance the electron density by their high positive indicative or mesomeric effect, whereby stronger chelation was formed and therefore the stability of the complexes.

ii) The low stability of HL_5 and HL_4 complexes can be attributed to the presence of the NO_2 and Cl groups in the p-position relative to the azo group, respectively. This is caused by the negative indicative effect of the NO_2 and Cl groups which decreases its ability for chelation and therefore the stability of the complexes.

iii) For the ligands with the same metal ion at constant temperature, the stability of the chelates increases in the order $HL_1>HL_2>HL_3>HL_4>HL_5$.[32]

Effect of Temperature The dissociation constants (pK^H) for azoquinoline and its substituted derivatives, as well as the stability constants of their complexes with Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} have been evaluated at 298, 308 and 318 K, and are given in Tables 2 and 4. The slope of the plot (pK^H or $\log K$ vs. $1/T$) was utilized to evaluate the enthalpy change (ΔH) for the dissociation or complexation process, respectively. From the free energy change (ΔG) and (ΔH) values one can deduce the entropy changes (ΔS) using the well known relationships (1) and (2):

$$\Delta G = -2.303 RT \log K \tag{1}$$

$$\Delta S = (\Delta H - \Delta G)/T \tag{2}$$

All thermodynamic parameters of the dissociation process of HL_3 and its derivatives are recorded in Table 2. From these results the following conclusions can be made:

i) The pK^H values decrease with increasing temperature, i.e., the acidity of the ligands increases, independent of the nature of the substituent.[33]

ii) A positive value of ΔH indicates that the process is

Table 4. Thermodynamic Functions for the Complexation of Substituted Quinoline Azodyes in 40% (v/v) DMF–Water Mixture at 298 K

Compound	M^{n+}	Free energy change (kJ mol^{-1})		Enthalpy change (kJ mol^{-1})		Entorpy change (J mol^{-1} K^{-1})	
		$-\Delta G_1$	$-\Delta G_2$	ΔH_1	ΔH_2	ΔS_1	ΔS_2
HL$_1$	Mn^{2+}	43.08	32.20	20.10	15.80	212.01	161.06
	Co^{2+}	43.90	32.60	13.88	15.32	193.89	160.80
	Ni^{2+}	44.20	32.90	15.80	16.75	201.33	166.62
	Cu^{2+}	45.07	34.17	16.75	13.88	207.46	161.24
HL$_2$	Mn^{2+}	41.90	31.20	21.53	16.75	212.85	160.92
	Co^{2+}	42.85	31.66	16.75	17.70	200.00	165.65
	Ni^{2+}	43.19	31.95	18.67	17.70	207.58	166.62
	Cu^{2+}	44.04	33.15	21.05	18.66	218.43	173.86
HL$_3$	Mn^{2+}	41.08	30.40	21.06	21.54	208.52	174.30
	Co^{2+}	41.80	30.80	21.99	21.03	214.06	173.94
	Ni^{2+}	42.28	31.26	21.06	22.02	212.55	178.79
	Cu^{2+}	43.36	32.50	18.67	21.54	208.15	181.34
HL$_4$	Mn^{2+}	38.85	28.20	29.19	27.75	228.31	187.75
	Co^{2+}	39.65	28.80	35.41	26.32	251.86	184.95
	Ni^{2+}	40.28	29.40	31.10	23.92	239.53	178.93
	Cu^{2+}	41.36	30.46	29.66	22.01	238.34	176.07
HL$_5$	Mn^{2+}	38.60	27.90	20.58	19.63	198.60	159.48
	Co^{2+}	39.08	28.20	21.54	19.63	203.42	160.49
	Ni^{2+}	39.88	28.87	21.54	18.67	206.11	159.52
	Cu^{2+}	41.08	29.67	20.58	19.15	206.92	163.82

endothermic.

iii)   A large positive value of ΔG indicates that the dissociation process is not spontaneous.

iv)   The dissociation processes for HL$_3$ and its derivatives have negative values of ΔS due to increased order as a result of the solvation processes.

All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in Table 4. It is known that the divalent metal ions exist in solution as octahedrally hydrated species and the obtained values of ΔH and ΔS can then be considered as the sum of two contributions : a) release of H$_2$O molecules, and b) metal–ligand bond formation. Examination of these values shows that:

i)   The stepwise stability constants ($\log K_1$, $\log K_2$) for ligand complexes increases with increasing temperature, *i.e.*, its stability constants increase with increasing the temperature.

ii)   The negative value of ΔG for the complexation process suggests the spontaneous nature of such process.[9,23]

iii)   The ΔH values are positive, meaning that these processes are endothermic and favourable at higher temperature.

iv)   The ΔS values for the ligand complexes are positive, confirming that the complex formation is entropically favourable.

Conductometric Studies. Stoichiometries   Stoichiometries of the complexes of ligands with Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} result from the conductometric measurements. These studies were carried out to investigate the stoichiometries of the formed complexes which denoting the formation of 1:1 and 1:2 (metal:ligand) complexes. The increase in conductance upon titrating metal ions by ligand is probably due to the liberation of the hydrogen ions from the OH during the complex formation.[9] The decrease in the conductance value occurs due to i) the increase of the volume of the metal ion chelate formation which is accompanied with decrease in the value of the diffusion coefficient of the particle, ii) the lowering of the charge on the metal ion through covalent bond formation with the ligand.

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