



Spectral and Thermodynamic Studies of Schiff Base Hydrazone Derivatives Complexes with Some Transition Elements

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A new hydration Schiff base consisting of 7-chloro-4-(*o*-hydroxy benzilidenehydrazo)quinoline with some divalent metal ions *viz.*, Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes were studied spectrophotometrically which obeyed Beer's law up to certain values, 6.6×10^3 , 8.0×10^3 dm³ mol⁻¹ cm⁻¹, respectively, indicating that the Schiff base ligand could be used to detect Co(II) and Ni(II) in such concentrations. The study was performed also for Fe(III)-complexes. Conductance and thermodynamically used molar ratio method to determine the stoichiometry of the complexes obtained confirmed the formation of 1:1 and 1:2, M:L complexes. The standard thermodynamic parameters *viz.* ΔG , ΔH and ΔS , for the proton-legend and the stepwise metal-ligand complexes were analyzed in terms of the electrostatic (eel) and non-electrostatic (crates, c) components. ΔH_c was found to be linearly correlated with the acceptor number of the metal ion (AN_M) and ΔH_{el} was linearly correlated with the ionic radii of the metal ion. The calculated values for ΔG° , ΔH° and ΔS° concluded that the complexation process processed spontaneously.

Keywords: Hydrazone, Spectro-potentiality, Transition metal complexes, Thermodynamic parameters.

INTRODUCTION

Hydration Schiff base compounds containing quinoline moiety are well known in natural materials and show interesting biological and antiviral activities¹⁻³. Many derivatives of hydration compounds form coloured complexes with different metal ions and can be used as analytical reagents for their determinations⁴⁻⁹. The coordination compounds of aroylhydrazones have been reported to act as enzyme inhibitors¹⁰ and are useful due to their pharmacological applications¹¹⁻¹³. The study of Schiff base hydrazones has been growing interest because of their antimicrobial, antituberculosis and antitumor activity¹⁻¹². The azomethine (C=N) linkage in Schiff bases imports in elucidating the mechanism of transmission and reexamination reactions in biological system¹⁴. The importance of metals and transition elements are formed organic compound due to its presence in many of the enzymes associated with mineral particles of large ring molecules such as hem¹⁵. Effect of the nature of the center metal ion and the medium, composition of fixed factors on the stability of the complexes formed hydrazones of Schiff bases with ions transition elements were studied by using, spectral studies of solutions and reduced the pollution of both heavy metals or undesired organic compounds.

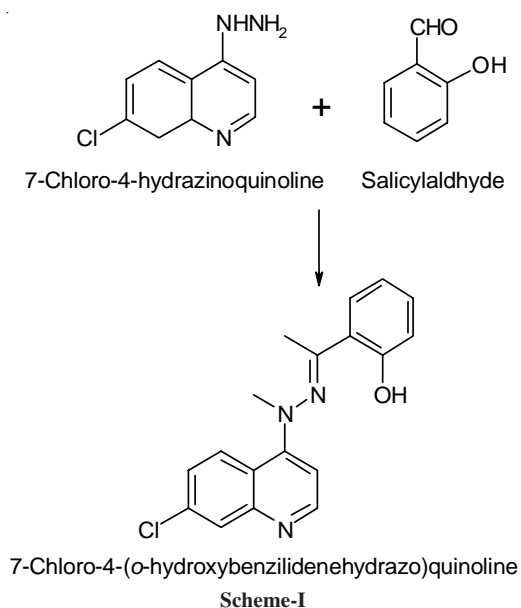
Thermodynamic parameters are computed and analyzed in order to investigate the bond character between the metal ligand. The magnetic moments and electrical conductance of the complexes were also determined.

EXPERIMENTAL

All chemicals used were for AnalR grade and the solutions of metal nitrates of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions were prepared in carbonate free double distilled water and they were stabilized using EDTA titrations¹⁶. The HL ligand was prepared as described previously¹⁷. The structure of the ligand was elucidated by IR, mass, ¹H NMR and electronic (UV-visible) spectroscopy, as well as micro analytical analyses¹⁷. The results have already been published¹⁷ and weighed quantity of the ligand was dissolved in 75 % (v/v) ethanol-water medium. Ethanol-water was freshly refluxed and distilled over magnesium powder and iodine¹⁶.

Synthesis of ligand: 7-Chloro-4-hydrazinoquinoline (2 g, 1 mmol) was dissolved in 10 mL absolute ethanol. To this solution 13 mL of salicylaldehyde (1.1 mmol) was added. The reaction mixture was refluxed for 2 h. After cooling, the yellow precipitate was collected, filtered and finally washed with

5-10 mL absolute ethanol and purified by recrystallization from ethanol (yield 80 % m.m.p.: 235 °C) (**Scheme-I**).



Electrical conductance conducted measurements using a WTW. D 8120 Weilheim LF. 42. Spectral measurements were conducted, on a Shimadzu Model UV-probe. A Hanna pH-meter Model 302 digital with conventional pH-electrode assembly was used for pH measurements at 10, 20, 30 and 40 °C. The ionic strength of the medium was kept virtually constant at 0.05 mol dm⁻³ with KNO₃ as background electrolyte. The temperature was maintained constant by use of double-jacket cells with water circulated from a constant-temperature bath. Purified nitrogen gas was bubbled through the solution before and during the titrations. Multiple titrations were carried out for each system and the pH meter readings were recorded⁶⁻⁹. Electronic absorption spectra of the free ligand and its complexes in 75 % (v/v) ethanol-water was recorded using a Shimadzu Model UV-probe spectrophotometer. The composition of the complexes in solutions was determined by the molar ratio method^{18,19}.

RESULTS AND DISCUSSION

Thermodynamic parameters: Thermodynamic parameters (Table-1) are calculated from the formation constants in a mixture of 75 % ethanol-water, at different temperatures as follows:

Free energy change ΔG°

$$-\Delta G^\circ = 2.2303T \log K \quad (1)$$

van-Hoff isotherm ΔH°

$$d \log K / dt = \Delta H^\circ / 4.57T \quad (2)$$

By solving (eqn. 1 and 2) we obtained

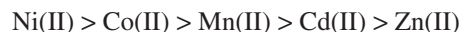
$$\log K = -\Delta H^\circ / 4.47T + \text{constant}$$

By plotting the relation between $\log K$ vs. $1/T$ we obtained a straight line its slope is equal to $-\Delta H^\circ / 4.57 T$ and ΔH° is in cal mol⁻¹.

The change in entropy (ΔS°) is calculated from Gibbs-Helmholtz equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Thermodynamic parameters provide valuable information about the nature of forming complexes, the degree of covalent bonding and the change in hydration. The thermodynamic parameters results and the stability constants of the metal ions at a temperature 30 °C in 75 % (v/v) prove that the stability constants of complexes ligand $\log K_1$ would be in the following order:



The Fe(III) ion was excluded because it must be compared with Triple charges ions. If we compare {Zn(II), Cd(II)} ions and {Co(II), Ni(II)} ions, we find that their positions are consistent with previous publication research²⁰⁻²⁴. Fig. 1 illustrates the form of a linear relationship between the dissociation constant of ligand and static stability of the complexes $\log K_1$. This linear relationship reflects the similarity of the ionic nature of the reaction between the metal and ligand²¹.

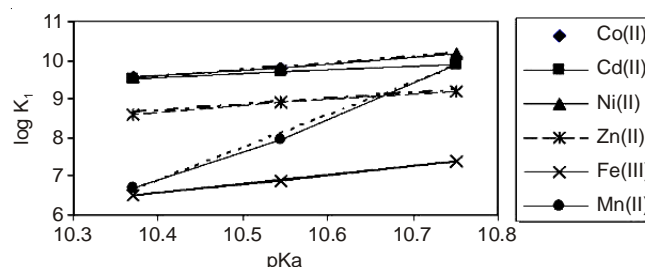


Fig. 1. Relationship between the values of $\log K_1$ and pK_a at 30 °C in 75 % (v/v) ethanol-water

We can also use functions to distinguish between thermodynamic parameters formed inside the outer sphere and inner sphere complexes. It reflects the function's thermodynamic

TABLE-1
THERMODYNAMICS FUNCTIONS AND STEPWISE FORMATION CONSTANTS OF 1:1 AND 1:2 METAL COMPLEXES AT 30, 40 AND 50 °C IN 75 % ETHANOL-WATER

Complex (HL)	30 °C		40 °C		50 °C		$-\Delta G^\circ_{30}$ (Kcal mol ⁻¹)		$-\Delta H^\circ_{30}$ (Kcal mol ⁻¹)		$-\Delta S^\circ_{30}$ (cal mol ⁻¹ K ⁻¹)	
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$-\Delta G^\circ_1$	$-\Delta G^\circ_2$	$-\Delta H^\circ_1$	$-\Delta H^\circ_2$	ΔS°_1	ΔS°_2
Co(II)	10.090	10.56	9.790	10.40	9.55	10.20	13.9903	14.6419	0.1208630	0.0803863	0.0457736	0.0480579
Cd(II)	9.880	10.99	9.690	10.60	9.52	10.10	13.6991	15.2381	0.0805280	0.1987040	0.0449457	0.0496351
Ni(II)	10.180	10.57	9.800	10.32	9.55	10.11	14.1150	14.6558	0.1411490	0.1029300	0.0461185	0.0480296
Zn(II)	9.210	9.69	8.930	9.31	8.61	9.00	12.7701	13.4356	0.1340380	0.1544200	0.0417032	0.0438324
Fe(III)	7.410	8.40	6.900	8.10	6.5	7.90	10.2743	11.6470	0.2036990	0.1120150	0.0332363	0.0380692
Mn(II)	9.910	10.61	7.960	10.47	6.7	10.30	13.7407	14.7113	0.7192720	0.0692309	0.0429749	0.0483235
pK_a	10.751	—	10.544	—	10.371	—	14.9068	—	0.0850294	—	0.0489166	—

parameters²⁵ and any type of these complexes may be as follows:

Therefore, the results confirm thermodynamic parameters which are internal complexes. Table-1 shows that the complexation process decreased with the increase of temperature, indicating that the temperature at least is the favourite for the complexation process and leading to negative values for ΔH° which means that the interaction between the metal ion and ligand molecule reaction is exothermic.

According to Nancollas and Degischer²⁶, the values of ΔH° reflect the change in the number and strength of the bonds that are formed by breaking during the interaction between the metal ion and ligand. The composition of the complex and hence the values of ΔH° is directly related to the type of interdependence between the metal ion (M^{n+}) and ligand molecules, as well as with the structure of complex formed. If we take into account the fact that the areas of crystal-fields produced by the consistency of oxygen centers O-coordinating sites are similar to the consistency of molecules²⁷, including water, ΔH° conclude that the effect is not affected by moving the replacement of water molecules. Therefore, the negative value of ΔH° is due to N-coordinating sites in the ligand molecule as described in the following structure:

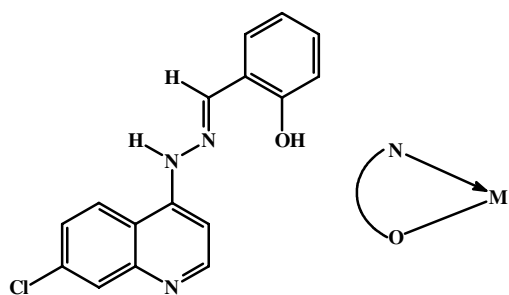


Table-2 shows the values of $-\Delta H_1^\circ > -\Delta H_2^\circ$ of the ligand complexes with ions Co(II), Ni(II), Fe(III) and Mn(II). This demonstrates that there is a change in the properties of X-rays of the ligand, change in the dentate character. In other words, the decline in values $-\Delta H_2^\circ$ indicated to change donor centers in ligand of tridentate (ONN) donor in 1:1 complexes to bidentate (ON) donor complexes to 1:2 (M:L) to overcome the steric hindrance in the complexes 1:1 (M:L). This is identical to the results of Evans *et al.*²⁸, where they obtained the same results. On the contrary, Table-2 illustrates that the values of $-\Delta H_2^\circ > -\Delta H_1^\circ$ for complexes with ions of Cd(II) and Zn(II) and takes

this as a characteristic sign of effect of *trans*-influence²⁹ of the second coordination.

In contrast, high negative values for ΔG° indicates that the complexity is spontaneously and that the positive values of ΔS° for all complexes are consistent with the hypothesis that during the process complexity remove a large number of water molecules with the possibility of changes in the number of coordination²⁹. This shows that the change in entropy reflects the formation of complexes. Fig. 2 shows the relationship between the change in ΔG_1° , ΔH_1° , ΔS_1° and the number of 3d electrons and found that relationship is between metal ions and the number of 3d electrons, which indicates that the change is a valuable thermodynamic parameters probably due to the change in the electron affinity to ions metals.

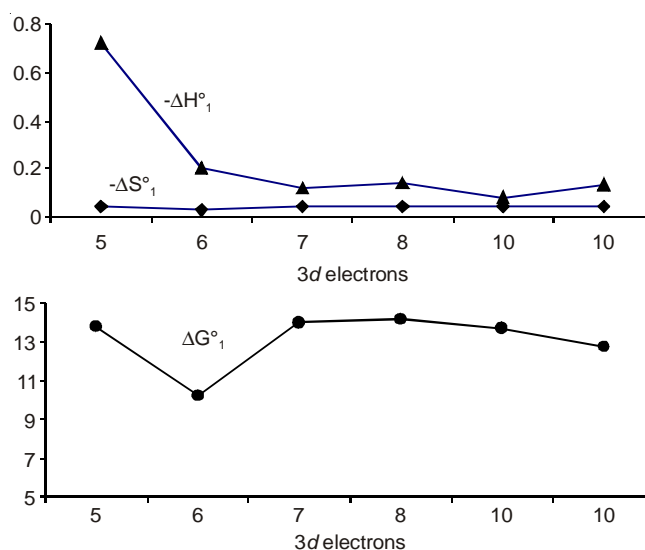


Fig. 2. Relationship between the thermodynamics functions, (ΔG_1° , ΔH_1°) and ΔS_1° and the 3d electrons

In order to get information on the nature of the bonds in the complexes, Table-3 would be advisable to analyze the values of ΔG° , ΔH° , ΔS° into two parts: (a) temperature-dependent ΔX_{et}° , electrostatic (el) interaction due to reaction of dipole or ion with long-range electrostatic forces of the powers of the electrostatic solvent medium. (b) non-dependent on temperature ΔX_{non}° non-electrostatic or also called Kratk ΔX_c° which is due to the molecule or ion is produced from a short term or short range of covalent bonds with the surrounding environment and hence

TABLE-2
THERMODYNAMICS FUNCTIONS AND STEPWISE FORMATION CONSTANTS OF 1:1 AND 1:2 METAL COMPLEXES AT 30, 40, AND 50 °C IN 75 % ETHANOL-WATER

Complex (HL)	30 °C		40 °C		50 °C		$-\Delta G_{30}^\circ$ (Kcal mol ⁻¹)		$-\Delta H_{30}^\circ$ (Kcal mol ⁻¹)		$-\Delta S_{30}^\circ$ (cal mol ⁻¹ K ⁻¹)	
	log K ₁	log K ₂	log K ₁	log K ₂	log K ₁	log K ₂	$-\Delta G_1^\circ$	$-\Delta G_2^\circ$	$-\Delta H_1^\circ$	$-\Delta H_2^\circ$	ΔS_1°	ΔS_2°
Co(II)	10.090	10.56	9.790	10.40	9.550	10.20	13.9903	14.6419	0.1208630	0.0803863	0.0457736	0.0480579
Cd(II)	9.880	10.99	9.690	10.60	9.520	10.10	13.6991	15.2381	0.0805280	0.1987040	0.0449457	0.0496351
Ni(II)	10.180	10.57	9.800	10.32	9.550	10.11	14.1150	14.6558	0.1411490	0.1029300	0.0461185	0.0480296
Zn(II)	9.210	9.69	8.930	9.31	8.610	9.00	12.7701	13.4356	0.1340380	0.1544200	0.0417032	0.0438324
Fe(III)	7.410	8.40	6.900	8.10	6.500	7.90	10.2743	11.6470	0.2036990	0.1120150	0.0332363	0.0380692
Mn(II)	9.910	10.61	7.960	10.47	6.700	10.30	13.7407	14.7113	0.7192720	0.0692309	0.0429749	0.0483235
pKa	10.751	—	10.544	—	10.371	—	14.9068	—	0.0850294	—	0.0489166	—

TABLE-3
ELECTROSTATIC (el) AND NON-ELECTROSTATIC THERMODYNAMIC PARAMETERS FOR
THE REACTION OF METAL IONS WITH HL LIGAND IN 75 % (v/v) ETHANOL-WATER AT 30 °C

Complex	ΔG°_{30} (Kcal mol ⁻¹)				ΔH°_{30} (Kcal mol ⁻¹)				ΔS°_{30} (cal mol ⁻¹ K ⁻¹)	
	$-\Delta G^\circ_{el}$		$-\Delta G^\circ_{non}$		$-\Delta H^\circ_{non}$		ΔH°_{el}		ΔS°_{el}	
	log K ₁	log K ₂	log K ₁	log K ₂	log K ₁	log K ₂	log K ₁	log K ₂	log K ₁	log K ₂
Co(II)	11.39590	11.88010	2.59440	2.76177	5.01251	5.17988	4.89164	5.09949	53.7543	56.0383
Cd(II)	11.22040	12.21450	2.47870	3.02360	4.89681	5.44171	4.81629	5.24301	52.9262	57.6155
Ni(II)	11.46890	11.87410	2.64602	2.78171	5.06413	5.19982	4.92298	5.09689	54.0987	56.0097
Zn(II)	10.533 00	10.98430	2.23716	2.45127	4.65526	4.86937	4.52123	4.71497	49.6838	51.8128
Fe(III)	8.73795	9.76253	1.53631	1.88442	3.98000	4.30252	3.75072	4.19052	41.2168	46.0497
Mn(II)	10.80260	11.93650	2.93815	2.77479	5.35626	5.19289	4.63697	5.12367	50.9557	56.3040

$$\Delta X^\circ_{non} = \Delta X^\circ_{el} + \Delta X^\circ_c$$

If we look at the degree of covalent bonding, we find that the ion metal has a softener donor³⁰. Fig. 3 shows the relationship between ΔH°_{non} and quantity $E_n^\#$ described by Klopman³⁰ as a measure of hardness and a softness, where we note that the metal ion soft features with negative values of high-value $E_n^\#$ and *vice versa*.

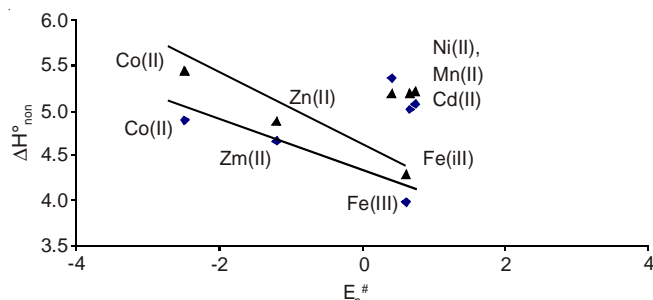


Fig. 3. Relationship of hardness and softness, $E_n^\#$ (eV), of metal ions and non-electrostatic heat change, ΔH°_{non} , of the formation of the complex

As is clear from the Fig. 3 that there is a linear relationship between ΔH°_{non} and the number of $E_n^\#$ ΔH°_{non} in the sense that increases as the increased softness of the softer metal ion. According to many authors³¹⁻³³, the change in electrostatic enthalpy ΔH°_{non} arises from changes that occur in the area of changes in the ligand field (LSF) associated with the composition of the complex. The following forms (Figs. 4-7) and after excluding the ion Fe(III), show the relationship between each of the electronegativity (X_m) and second ionization potential (2Ip) for ions metals with a fixed configuration log K₁ as well as with a fixed configuration log (K₁K₂) and note that the constants of the configuration log (K₁K₂) of the complexes are growing linearly with the increase electronegativity (X_m) or increase the ionization potential of the metal ion bilateral charge (2Ip).

This reflects the stability of the complexes are getting an increase of X_m and hence the link between the metal and ligand increase in the properties of covalent and confirmed by the linear relationship between ΔH_{non} and X_m (Fig. 8).

On the other hand, the property of the bond in covalent complexes can infer from the linear relationship (Fig. 9) between ΔH_{non} and AN_m acceptor number of the cations³⁴.

Acceptor number (AN) known as a quantitative measure of Lewis acidity according to the ability to form a covalent bond with a pair of electrons. We can summarize that ΔH°_{non}

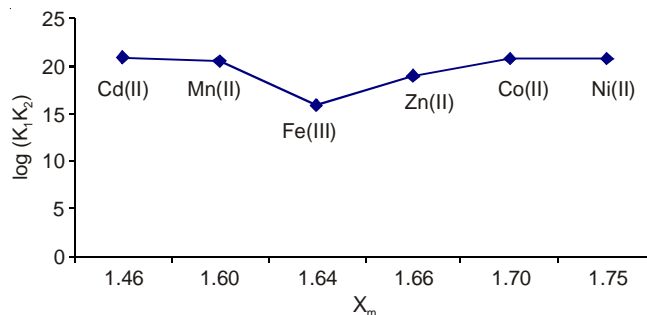


Fig. 4a. Relationship of the X_m of the metal ions with log (K₁K₂)

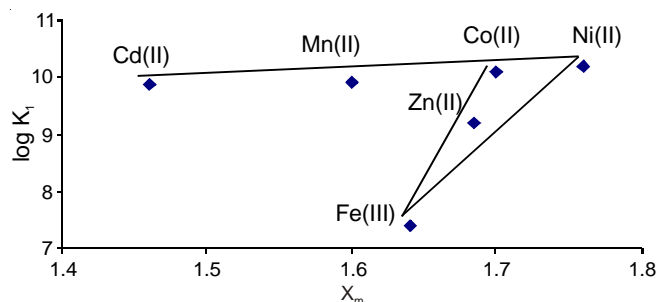


Fig. 4b. Relationship between the electronegativity of the metal ions

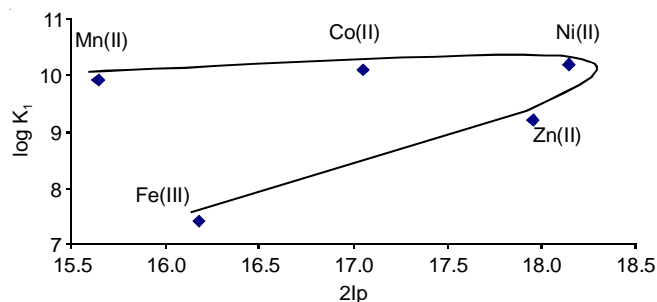


Fig. 5. Relationship and log K₁ with 2Ip including Fe(III)

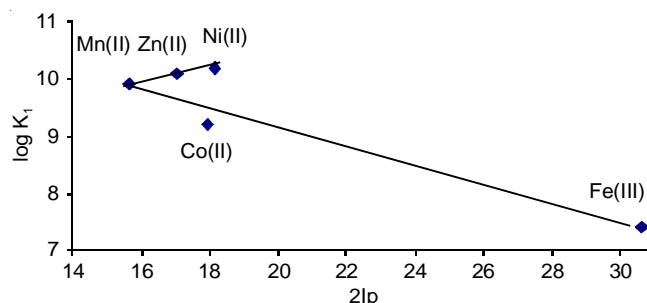


Fig. 6. Relationship and log K₁ with 2Ip including 3Ip of Fe(III)

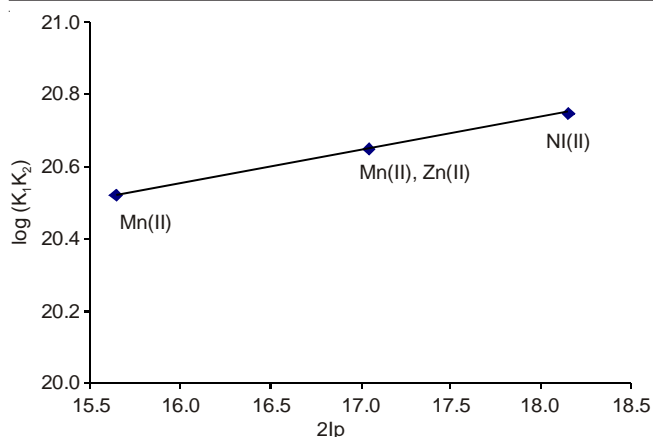


Fig. 7. Relationship of $\log (K_1K_2)$ with $2I_p$ of divalent cations excluding Fe(III)

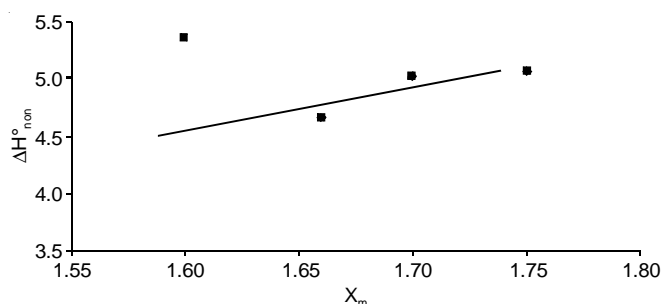


Fig. 8. Relationship of X_m of the metal ions with ΔH°_{non}

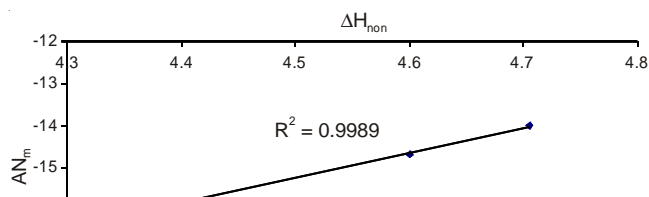


Fig. 9. Relationship of acceptor number of metal ions, AN_m , with ΔH°_{non}

associated with a positive relation with the donor acceptor number while ΔH°_{el} and ΔS°_{el} linked to a positive relation with half radii of metal ion (Figs. 10 and 11).

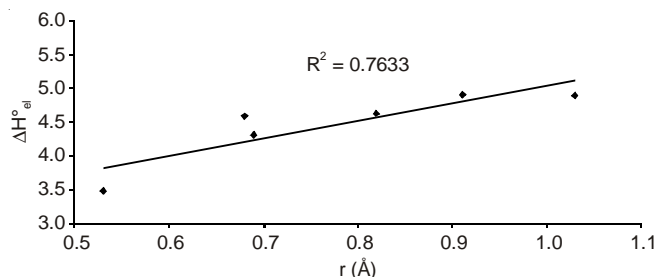


Fig. 10. Relationship of ΔH°_{el} with ionic radii of metal ions

Conductometric titration: In order to get information on the composition of complexes we have had adjustments electrical conductivity. It is known that this measurement shows that the measured amount reflect and directly proportional to the concentration of one or more of the ions. When the inter-

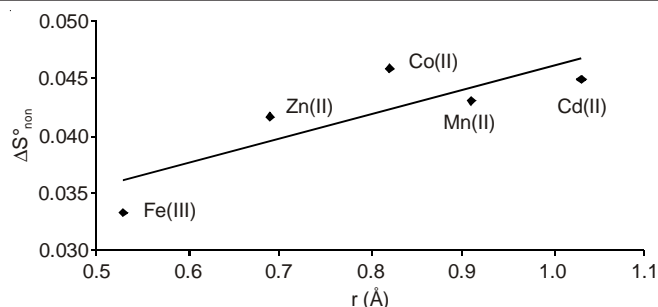


Fig. 11. Relationship of ΔS°_{non} with ionic radii of metal ions

action between metal ions and ligand we get calibration curve, which consists of two or more lines transmit at the equivalent point (the point that determine the structure of the complex)³⁵.

Fig. 12 showed the conductometric titration curve of ligand, HL, with metal ions, in which electrical conductivity increases continuously, whenever we add ligand to the metal ion and continue to increase until it reach the equivalence point for the titration. It is also clear that this behaviour was attributed to the replacement of some metal ions with some of complex molecules. On adding the following drop of ligand, it is noted that there is a slight increase in the values of electrical conductivity, which reflects that the added ligand remains without reaction and that increase could be due to the accumulation of ligand molecules. Titration curve and electrical conductivity appear to be complex double transmittance which reflects the ratio of M:2 L and M:L and corresponds with the results of potential titrations. Titration electrical conductivity has been made under the same conditions of potential titration.

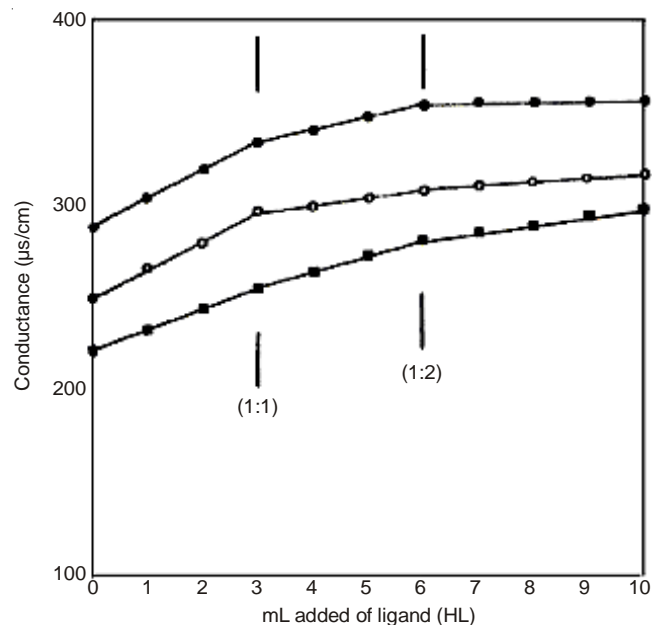
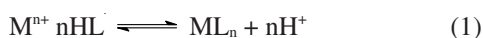


Fig. 12.

Spectrophotometric measurements: The spectra of organic molecules are usually affected by the nature of the solvent and observed the influence of peaks intensity and position of the absorption top λ_m . The influence depends on several factors, including, for example, the physical properties of solvent such as dielectric constant and the determination of the dipole moment and refractive index as well as the ability

of the solvent on the interaction through the formation of hydrogen bonds

Determination of stoichiometries of formed complex: The method used to determine the percentage molar ratio to form the complex.



$$K = \frac{[ML_n][H^+]^n}{[M^{n+}][HL]^n}$$

Job's method^{35,36} derived from eqn. 1, the interaction between the metal ion M^{n+} and organic ligand.

Molar ratio method³⁷⁻⁴⁰, where the metal ion concentration was constant while changing the concentration of [ligand]/[metal ion] and when we plot the values of absorption of these solutions against molarity ratio we get the straight lines intersect each two of them at a certain rate. And contrary to the method that we can make ligand concentration fixed and change the metal ion concentration was measured [metal ion]/[ligand] absorption of solutions at required pH.

Slope-ratio method in this way prepares two series of solutions. Saves in the first series ion concentration element constant while changing the ligand concentration. In the second series saves the ligand concentration ion concentration fixed and changes the element. The pH value of the two methods was constant and measured the absorption using both the contents of the standard solution except the ion element.

We used the molarity ratio method to determine the molarity ratio of the complexes Co(II)-ligand and Ni(II)-ligand as follows: the preparation of a series of solutions, measuring 10 mL consisting of 0.2 mL of a solution of concentration [2-10 M] of the ions Co(II), Ni(II) and Mn(II). Then added 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 mL of a solution of the ligand [2-10 M] added buffer (3 mL) and then to complete the 10 mL of 70 % (v/v) ethanol-water, when ionic strength $m = 0.5$ M and then measured the spectrum of the figure turns out to be ML1 and ML2 (Fig. 13). We discuss the spectra of the complex of Co(II)-ligand (as an example to the rest of the complexes) as a function of ligand concentration and analysis of the results at wavelengths different that the ions Co(II) and Ni(II) are two entities essential Two main complex species are 1:1 and 2:1 metal to the ligand.

$$n(CL)/n(CM)$$

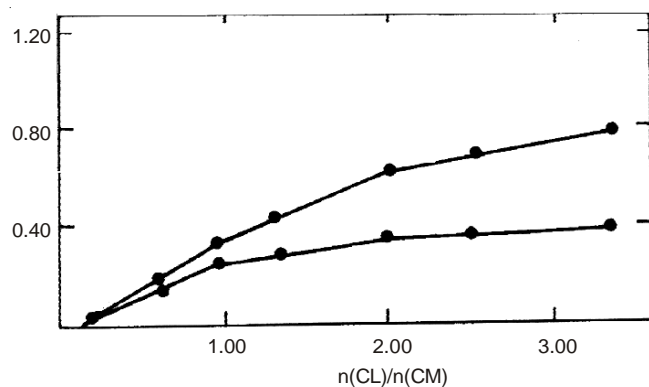


Fig. 13. Mole ratio method for Co(II)-ligand (a) and Ni(II)-ligand (b)

The results of this method agreed with the results of measuring the pH adjustments, where the Co(II), Ni(II), as an example to the rest from complexes, ML and ML₂ overlapped with ligand HL.

Validity of Beer's law: Using a constant concentration of ligand HL (1×10^{-3} M) and change the concentration of ions Co(II), Ni(II) and Mn(II) in a mixture of ethanol-water percentage of 75 % (v/v) and when the ionic strength ($= 0.05$ using potassium nitrate and ligand reference when $\lambda = 500$ nm and found that they all follow the Beer law of standard deviation 0.002, 0.006 and 0.003 respectively during the concentration of metal ion complexes with Co(II) of 1×10^{-5} WTWD-812 Weilneium-conductivity meter, model LBR, fitted with a cell model LTA100 to 4×10^{-4} M With Ni(II) and the values of molar absorptivity (ϵ) at 500 nm for the complexes of Co(II), Ni(II), Mn(II) are respectively 6.6×10^3 , 8.0×10^3 and 1.4×10^3 dm³ mol⁻¹ cm⁻¹, indicating that HL can be used as a sensitive factor in the specific analysis to determine the copper(II) and nickel(II) form (Fig. 14).

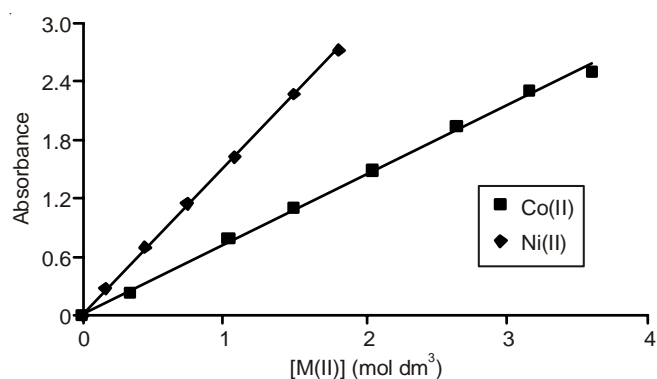
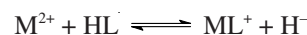
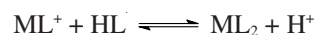


Fig. 14. Validity of Beer's law, (a) Co(II)-ligand at pH = 8; (b) Ni(II)-ligand at pH = 8

The pH metric titrations in 75 % (v/v) ethanol-water of the free ligand and its mixtures with the metal ions were carried out as described⁶⁻⁹. Using the equations of Irving and Rossoti²⁰ the curves were used to calculate the formation constants of the following equilibria:



and



The experimental reading was used to calculate the values of \bar{n} and PL. From which the stability constant $\log K_1$ and $\log K_2$ were calculated with the help of the following equations given by Irving and Rossoti²⁰.

$$\log \frac{\bar{n}}{1-\bar{n}} = \log K_1 + pL$$

$$\log \frac{\bar{n}-1}{2-\bar{n}} = \log K_2 + pL$$

The metal-ligand stability constant was obtained using a linear plot method by plotting $\log \frac{\bar{n}}{1-\bar{n}}$ or $\log \frac{\bar{n}-1}{1-\bar{n}}$ against $\log k$. Where \bar{n} is defined by Irving and Rossetti²⁰ as the

average number of the reagent molecules attached per metal ions. It can be obtained from the following relations

$$\bar{n} = \frac{(V_3 - V_2)(N^0 + E^0)}{(V^0 + V_2)\bar{n}_A TC_M^0}$$

and

$$pL = \log_{10} \frac{\sum_{n=0}^{n=1} \beta_n^H \left(\frac{1}{\text{anti log pH}} \right) V^0 + V_2}{TC_L^0 - \bar{n} TC_M^0}$$

where V_2 and V_3 are the volumes of alkali required to reach the same pH value, V_0 is the total volume of titrating mixture, N^0 and E^0 are the concentration of free acid, respectively, TC_L^0 and TC_M^0 are the total concentration of ligand and metal ion, respectively and pL , is the free ligand exponent. The experimental reading was used to calculate the values of \bar{n} . From which the stability constant $\log K_1$ and $\log K_2$ were calculated with the help of the following equations given by Irving and Rossetti²⁰.

The variations of pKH , $\log K_1$ and $\log K_2$ vs. $1/T$ gave straight lines which enable us to calculate the thermodynamic parameters ΔG° , ΔH° and ΔS° of the complex formation by the vant-Hoff equation and other relationships^{21,22}. Conductometric titrations were carried out at room temperature by titrating 30 mL metal ion solution (1×10^{-3} mol dm^{-3}) with the ligand solution (1×10^{-2} mol dm^{-3}).

Conclusion

The present work describes the complex formation equilibria was investigated to ascertain the composition and stability constants of the complexes. The effect of ligand properties on the stability of the complexes was investigated. After tracing the complexation properties of discrete ligands towards different metals, it is also more easy to correlate the data to the origin matter. As phenolic acids are a significant part of the chemical structure of substances it can be postulated, from the data obtained, that they can have an important role in their complication properties, mainly due to the presence of a hydroxyl group. To note that the discrete ligands used in previous studies only possess a phenolic function, usually in a *ortho*-position.

From the results obtained one can propose this type of structure corresponds to suitable discrete ligands. Owing to their natural origin, phenolic acids could also be proposed, as the stability constants were found to be rather high. The protonation constants (pK_1 and pK_2) were determined by Irving-Rossetti pH titration technique. Also metal-ligand stability constants of their complexes with metal ions (Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} , Zn^{2+} , Cd^{2+} and Fe^{3+}) have been determined potentiometrically. It appears that the present ligand is a better complexing agent with metal ions compared with the order: $\text{Mn(II)} < \text{Co(II)} < \text{Ni(II)} < \text{Cu(II)} < \text{Zn(II)} < \text{Cd(II)} < \text{Fe(III)}$. The corresponding thermodynamic parameters (ΔG , ΔH and ΔS) were derived and discussed the dissociation process is non-spontaneous.

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