

Thermodynamic of Complexation of Lanthanides and Some Transition Metal Ions by 3,5-Dinitro-2'-Hydroxy Benzanilide

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The stepwise stability constants of (MHL) and (ML) complexes between transition (Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} , Cd^{2+}) and lanthanide ions and 3,5-dinitro-2'-hydroxy benzanilide (DHBH) in 75% (v/v) dioxane-water at constant ionic strength (0.01 M KNO_3) were determined at different temperatures. The thermodynamic parameters for the proton-ligand and metal-ligand stability constants were obtained by the temperature coefficient method. The plot of thermodynamic parameters vs. ionic potential (Z^2/r) of the lanthanide elements is not linear as expected from ionic theory. The obtained data support the interpretation of the expanded solvation sphere through the lanthanide series. Anomalies in chelating tendencies at gadolinium indicate a type of cross-over point at which solvent-metal and ligand-metal interaction may occur. Spectrophotometric studies were carried out for Cu^{2+} , Ni^{2+} and Co^{2+} -DHB complexes. The solid complexes were isolated and characterized by elemental analysis, conductance, magnetic properties and infra-red spectra.

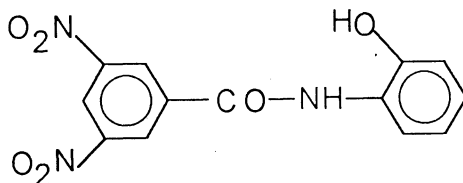
INTRODUCTION

A survey of literature shows that acetoacetanilide¹ and its derivatives² were used as organic chelating agents with different metal ions. The formation of complex compounds of acetoacetanilide, benzoylacetanilide and their derivatives with Cr^{3+} was also studied³. In the present study, the stability constants of Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} , Cd^{2+} and Ln^{3+} with 3,5-dinitro-2'-hydroxy benzanilide (DHBH) were determined potentiometrically at different temperatures. Also, the thermodynamic parameters of complexation were calculated from the temperature dependence of the stability constants. Spectrophotometric studies for Cu^{2+} , Ni^{2+} and Co^{2+} -DHB complexes were carried out. Also, their solid complexes were separated and their infrared spectra are discussed. Finally, the elemental analysis, molar conductance measurements and magnetic moment results support those obtained potentiometrically.

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EXPERIMENTAL

The solid ligand DHBH was prepared by mixing 0.01 mole of 3,5-dinitro benzoyl chloride and 0.01 mole *o*-aminophenol in dimethyl formamide (20 mL). The mixture was refluxed for 15 min. The solid obtained was filtered off and recrystallized from ethanol to give the pure DHBH (I).



(I)

Stock solutions of the metal nitrates were prepared and standardized using EDTA in the presence of a suitable indicator⁴. Purification of dioxane was carried out as described earlier⁵. The experimental techniques used in the present investigation were the same as reported previously⁵⁻⁷.

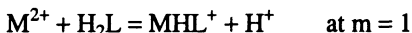
RESULTS AND DISCUSSION

pH-metric study: The potentiometric titration curve of DHBH is shown in Fig. 1. One proton dissociates from phenolic group between $m = 0$ and $m = 1$ (where m is the number of moles of base added per mole of ligand present). At higher pH values, an additional proton dissociates from anilide ($-\text{NH}-$) group. For the general protonation equilibrium:



The constant K_n^{H} was determined as described previously⁸.

Representative plots of the curves of DHBH with 2 : 1 molar ratios of ligand to metal ions are shown in Fig. 1. The titration curves in presence of metal ions (Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} and Cd^{2+}) show two buffer regions. The first is between $m = 0$ and $m = 1$ and the second one is between $m = 1$ and $m = 2$ due to the stepwise formation of protonated $[\text{MHL}]^+$ and the neutral $[\text{ML}]$ type complexes.



The above view agrees with that reported by Kabadi *et al.*⁹ for the complexes formed between salicylanilide and some transition metal ions.

The titration curves of DHBH in presence of Ln^{3+} showed precipitation occurring at $\text{pH} = 6.5$, followed by inflection at $m = 2-3$; this may be due to the hydrolysis of $[\text{MHL}]^{2+}$; thus the formation constant for only protonated complex is calculated. Values of $\log K_1$ for protonated and non-protonated complexes were calculated with the help of the expression given by Irving and Rossotti¹⁰.

$$\log n'/(1 - n') = \log K_1 + \text{pL} \quad (1)$$

where n' is the number of ligands bound by one metal atom and ranged between 0.1-0.8.

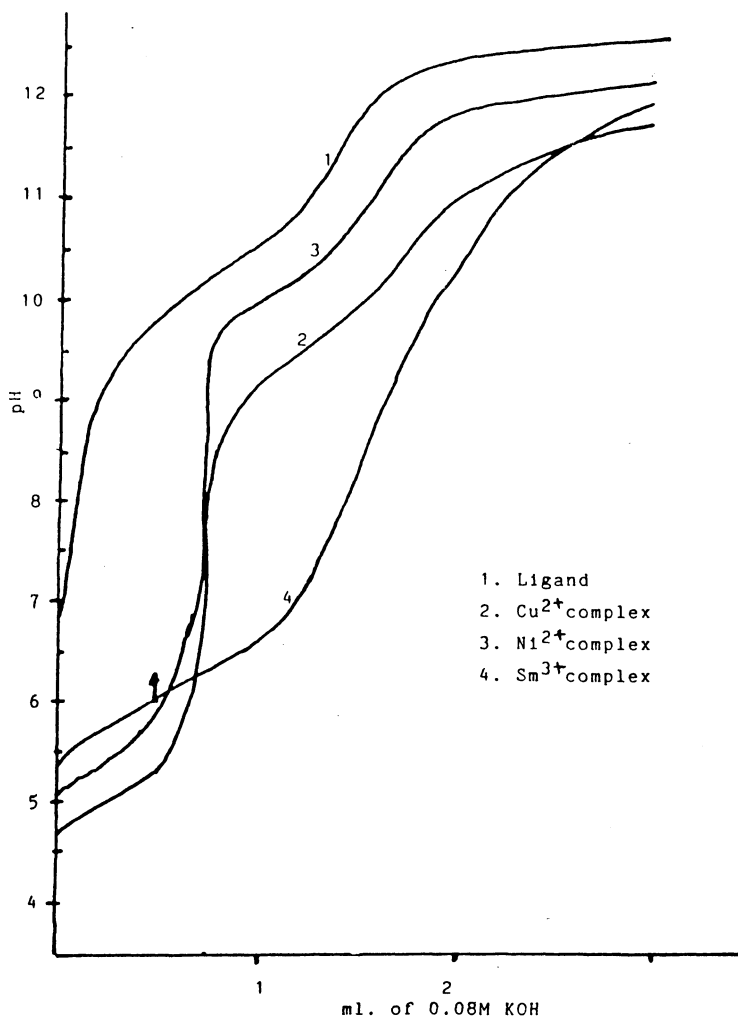


Fig. 1 Potentiometric titration curves for DBDH complexes in 75% dioxane-water at 30°C

This relation was solved graphically using the plots of $\log [n'/(1 - n')]$ vs. pL. These plots give straight lines whose interception with the pL axis gives $\log K_1$. The values of the constants were refined using least square method and given in Table-1

The change of pK_1^{H} and pK_2^{H} with $1/T$ was checked using linear regression method, and always gave straight line with correlation coefficient (R) equal to 0.980. This indicates that raising of temperature increases the acidity of the ligand. The linear change of the stability constants with $(1/T)$ permits the calculation of the enthalpy of the complexation process in accordance with the Van't Hoff equation:

$$\log K = -(\Delta H/2.303 RT) + \text{constant} \quad (2)$$

TABLE-1
STABILITY CONSTANTS OF METAL CHELATES OF DHBH
AT DIFFERENT TEMPERATURES
($\mu = 0.1 \text{ M KNO}_3$; 75% dioxane-water)

Cation	log K_{MHL}				log K_{ML}				M^{3+}	log K_{MHL}			
	10°C	20°C	30°C	40°C	10°C	20°C	30°C	40°C		10°C	20°C	30°C	40°C
H ⁺	10.18	9.99	9.84	9.67	11.41	11.16	11.05	10.87	La	6.15	5.86	5.58	5.25
Cu ²⁺	8.48	8.02	7.44	7.08	5.45	5.08	4.55	4.18	Ce	6.36	6.08	5.80	5.54
Ni ²⁺	8.18	7.63	7.10	6.80	4.38	4.02	3.66	3.40	Pr	6.30	6.02	5.73	5.40
Co ²⁺	7.85	7.40	6.98	6.55	4.05	3.80	3.58	3.25	Nd	6.50	6.28	5.91	5.62
Zn ²⁺	7.35	7.05	6.60	6.20	3.96	3.75	3.59	3.15	Sm	6.78	6.54	6.22	5.89
Mn ²⁺	7.02	6.62	6.18	5.94	3.87	3.68	3.45	3.10	Eu	6.93	6.70	6.45	6.06
Cd ²⁺	6.88	6.45	6.12	5.78	3.80	3.60	3.40	3.04	Gd	6.72	6.50	6.20	5.83
									Tb	6.89	6.68	6.33	5.95
									Dy	7.15	6.78	6.49	6.20
									Ho	7.36	6.99	6.73	6.45
									Er	7.57	7.35	6.98	6.69
									Tm	7.79	7.56	7.28	6.92
									Yb	7.92	7.84	7.49	7.16
Lu	7.99	7.92	7.62	7.34									

Error limits $\pm(0.01-0.09)$

Least squares analysis was used to calculate ΔH and the probable error in enthalpy terms. Also, the free energy ΔG and entropy change ΔS are calculated. The calculated thermodynamic parameters are given in Table-2. ΔG values have been found to be negative in all cases, showing that the formation of complexes is a spontaneous process. ΔG values have been found to increase with increasing temperature indicating that complexation favours low temperature. This is also confirmed by negative enthalpy values.

Fig. 2 shows a plot of ΔG vs. ΔH for the chelates of DHBH. It can be seen that these relations are roughly linear. This is to say that the entropy changes of the reactions have caused no usual effects within the chelates of a given reagent. It is reasonable to assume that this will generally be true, therefore the entropy of a series of chelation reactions with a given reagent will be either roughly constant or vary regularly. This accounts for the widespread success of log K_1 vs. second ionization potential (2 Ip). Each time this relation is used, it is implicitly assumed that only bond strength or ΔH is involved. Since the second ionization potential may be taken as a rough estimation of the average electron attracting power of a divalent metal ion for a source of electron such as that found in the chelate groups, hence it is more nearly related to bond energy and ΔH of chelation than to ΔG as measured by log K . It is also to be noted that ΔH should be more

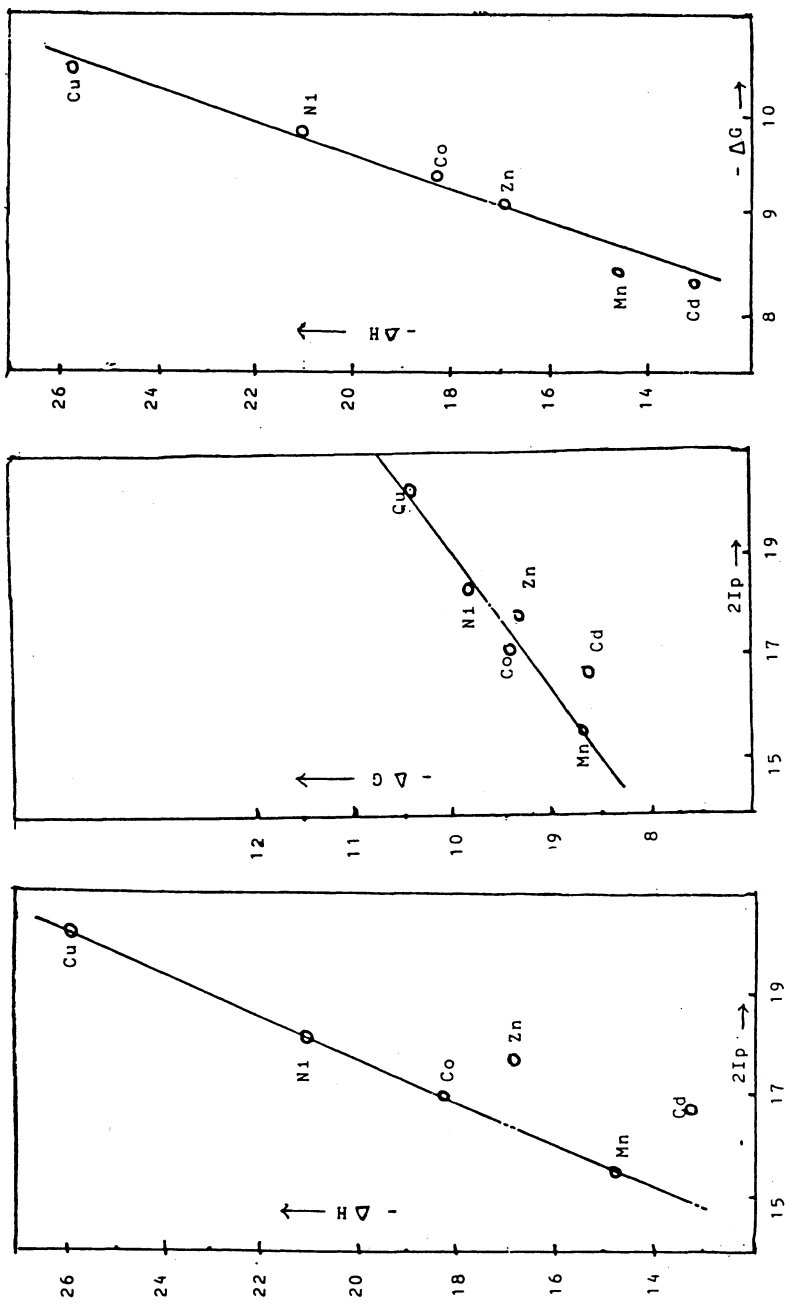


Fig. 2 Correlation between $\Delta G/\Delta H$ second ionization potential (2Ip) for the chelates of DHBH

sensitive index of bond strength than ΔG . Fig. 2 shows a plot of 2 Ip of the gaseous metal against ΔH and ΔG of chelation. As can be seen the relationship is satisfactory. This order is in good agreement with that reported by Irving¹¹.

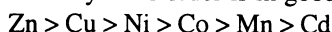


TABLE-2
THERMODYNAMIC DATA FOR M^{2+} -DHBH AND Ln^{3+} -DHBH COMPLEXES AT 30°C
($\mu = 0.1 \text{ M KNO}_3$; 75% dioxane-water; ΔG , ΔH in kcal/mol and ΔS in cal/mol/deg)

Cation	(MHL)			(ML)			M^{3+}	(MHL)		
	$-\Delta G$	$-\Delta H^a$	$-\Delta S^b$	$-\Delta G$	$-\Delta H^a$	$-\Delta S^b$		$-\Delta G$	$-\Delta H^a$	$-\Delta S^b$
H^+	-13.37	-6.28	23.40	-15.42	-7.68	25.56	La	7.79	14.66	22.66
Cu^{2+}	10.38	25.82	50.95	6.35	19.96	44.92	Ce	8.10	18.15	33.15
Ni^{2+}	9.91	20.94	32.63	5.11	13.26	26.90	Pr	8.00	13.96	19.66
Co^{2+}	9.49	18.15	28.56	5.00	11.37	21.02	Nd	8.25	15.77	24.83
Zn^{2+}	9.21	16.75	24.88	4.91	10.47	18.33	Sm	8.68	15.35	22.02
Mn^{2+}	8.63	14.66	19.90	4.82	9.21	14.51	Eu	9.00	14.66	18.65
Cd^{2+}	8.54	13.02	14.77	4.75	8.38	11.98	Gd	8.65	16.47	25.81
							Tb	8.83	17.45	28.44
							Dy	9.06	17.87	29.06
							Ho	9.39	18.24	29.82
							Er	9.74	18.24	28.66
							Tm	10.16	18.56	27.74
							Yb	10.45	18.15	25.40
							Lu	10.64	19.12	28.00

^a $\pm(0.13 - 0.68) \text{ kcal/mol}^{-1}$; ^b $\pm(0.4 - 1.6) \text{ cal mol}^{-1} \text{ deg}^{-1}$.

This behaviour may be attributed to the presence of both nitrogen and oxygen coordination centers in the ligand.

The thermodynamic parameters of complexation of the lanthanides with DHBH as a function of the ionic potential Z^2/r (r is the cationic radius of the lanthanide element) are plotted. On electrostatic basis, the strength of the bonds formed between metal ion and ligand would be expected to be fairly closely related to cation size. This energy might be expected to increase almost linearly as the radius of the ion decreases through the series. This expected behaviour is not observed for the lanthanide series. The ΔG , ΔH and ΔS plots have discontinuities in the middle of the series "gadolinium break". This behaviour has been attributed to a structural change in the hydration sphere of the lanthanide ions near the middle of the series¹²⁻¹⁴.

In solvation¹⁵, the majority of the data support a change in hydration number across the lanthanide series. The light lanthanides (La-Nd) form a series with a

hydration number of nine (primary sphere) and a tricapped trigonal prism (TCTP) geometry, whereas the heavier elements (Tb-Lu) apparently form octahydrates with square antiprismatic structures. For the hydrated ions in the middle of the series (Nd-Tb), there is either some type of transitional structure between these two geometries or both hydrate structures exist in rapid equilibrium. These conclusions are supported¹⁵ by data from X-ray and neutron diffraction, from fluorescence, Raman and visible spectroscopy and from thermodynamic and exchange kinetics. They are also in agreement with data on the apparent molal volumes, relative viscosities, molar heat capacities, heat of dilution, electrical conductance and entropies of hydration. Plots of these properties as a function of the lanthanide ionic radius show the general pattern of "S-shape" from La to Lu. The only exception was with Ce(III), and the anomalous behaviour is probably due to the tendency of cerium towards quadrivalency.

The entropy values given in Table-2 are negative for all M^{2+} -DHB complexes. Such negative entropy change can be attributed to the extensive solvation of metal chelates in aqueous organic medium. This may be due to the exposure of the polar oxygen, nitrogen and the metal ion of the chelate to solvent molecule¹⁶. The negative stepwise entropy changes observed for DHBH metal chelates in 75% (v/v) dioxane-water emphasize the predominance of the coordination process. Finally, the absence of 1 : 2 chelates in the present case may be due to steric hindrance produced by the attached ligand in the 1 : 1 chelate to the approach of the second one.

Spectrophotometric studies

Effect of pH on DHBH ligand: Fig. 3 shows the effect of pH on the spectrum of DHBH ligand; the isoelectric point at $\lambda = 470$ nm represents the conversion of the phenolic ($-\text{OH}$) to ($-\text{O}^-$) group, from which the dissociation constant (pK_1^{H}) of the ($-\text{OH}$) group was determined by applying the modified limiting absorbance method¹⁷. The result obtained ($\text{pK}_1^{\text{H}} = 1.025$) was in good agreement with that obtained from the potentiometric study.

Effect of pH on metal complexes: The effect of pH on the equilibrium constants for 1 : 2 Cu^{2+} -, Ni^{2+} - and Co^{2+} -DHB complexes has been studied. It was found that, the absorbance of the different complexes increases by increasing pH until $\text{pH} = 5.0-5.4$, $6.3-7.0$ and $6.5-7.2$ for Cu^{2+} , Ni^{2+} and Co^{2+} complexes, respectively. Then a sudden lowering of absorbances, after these pH's, may be due to the hydrolysis of unreacted metal or formation of other species.

Effect of DHBH concentration: On maintaining the metal ion concentration unchanged, while that of DHBH being varied as shown in Fig. 4 (a, b and c), the absorption spectra increases gradually with increasing DHBH concentration until (M : L) is equal to (1 : 2) for Cu^{2+} , Ni^{2+} and Co^{2+} complexes as a result of saturation (equilibrium) attainment.

Stoichiometry of complexes: The compositions of Cu^{2+} , Ni^{2+} and Co^{2+} complexes were studied in non-buffered solutions at $\text{pH} = 5.5$ for Cu^{2+} , $\text{pH} = 7$ for Ni^{2+} and Co^{2+} complexes in 75% dioxane-water applying the molar ratio method¹⁸. The method denotes the formation of 1 : 2 (M : L) complexes. The apparent formation constants of complexes of Cu^{2+} , Ni^{2+} and Co^{2+} were deter-

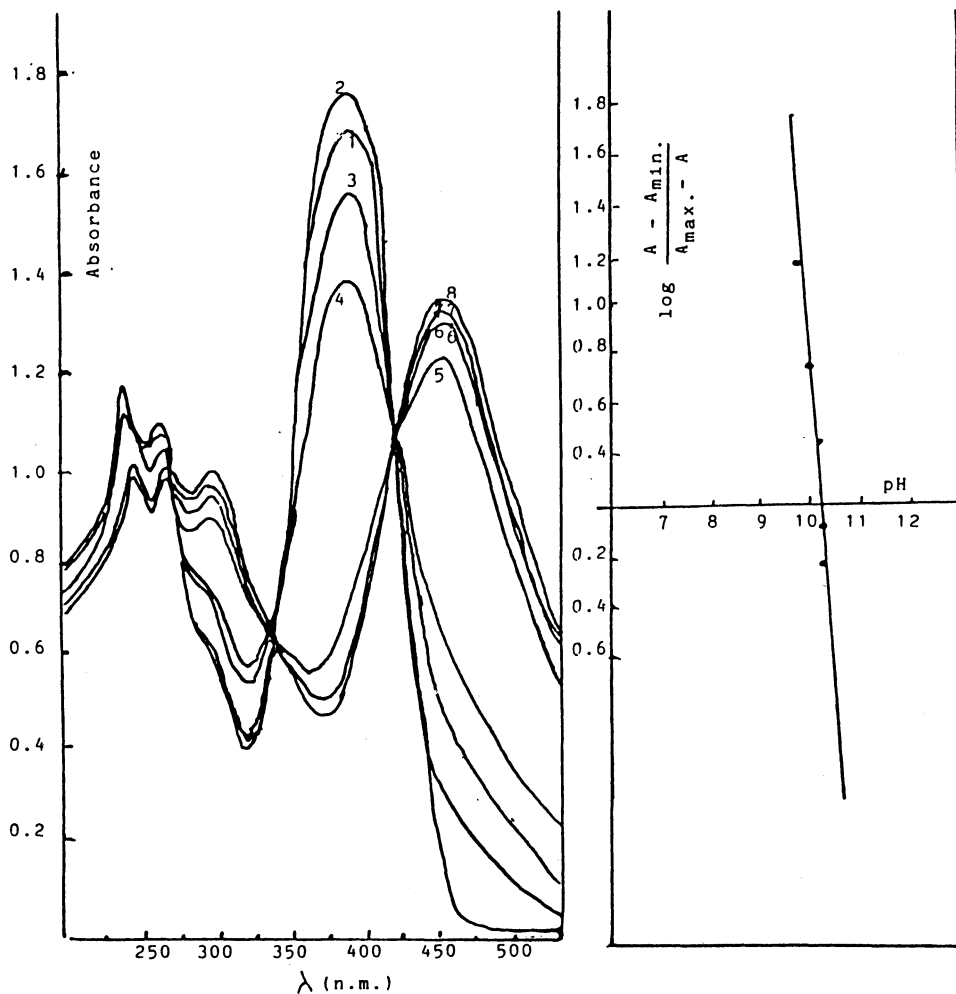


Fig. 3 Spectrophotometric study of DHBH ligand at different pH and calculation of (pK_1^H) by modified limiting method

mined from the results of the spectrophotometric data, with molar ratio²⁴ method by applying the relation:

$$K_f = \frac{(A/A_m)}{[1 - (A/A_m)]^{(1+n)} \cdot n^2 \cdot [L]^n}$$

where, K_f is the apparent formation constant of the complex

A is absorbance at a given ligand concentration $[L]$

A_m is limiting absorbance value and

n is the stoichiometric ratio (number of ligands in the chelate molecule).

The apparent formation constants obtained for Cu^{2+} , Ni^{2+} and Co^{2+} complexes are $\log K_f = 5.290, 4.261$ and 3.821 respectively.

The electronic spectra of the solid complex of Cu^{2+} in DMF show one broad band (570–610 nm) with λ_{max} at 590 nm. The band can be assigned to

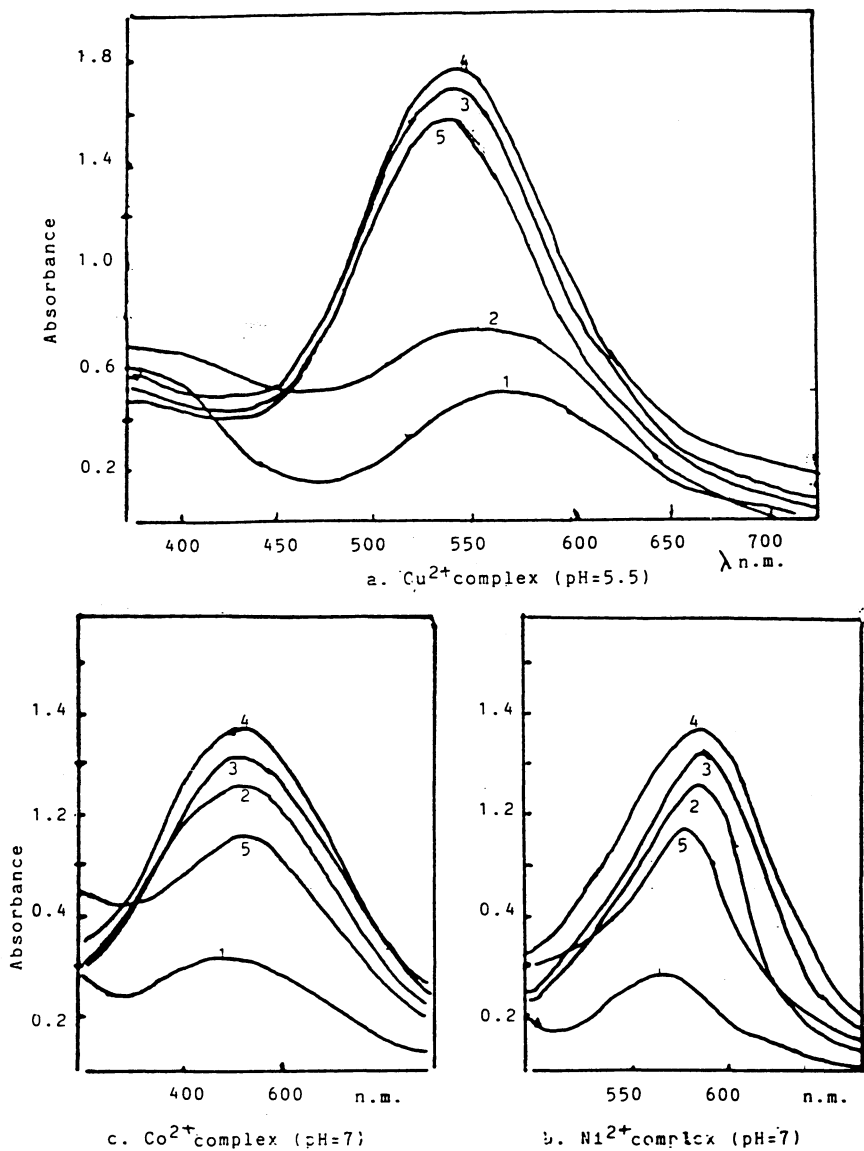


Fig. 4 Effect of changing ligand concentration on the formed complexes:

- | | | |
|----------|--------|----------|
| 1. 1:0.5 | 2. 1:1 | 3. 1:1.5 |
| 4. 1:2 | 5. 1:3 | |

${}^2E_g \rightarrow {}^2T_{2g}$ transition. The position of λ_{\max} and sharpness of the band indicate a square planar geometry for Cu^{2+} -complex. For Ni^{2+} -complex, the spectra show a shoulder band at λ_{\max} (595–610 nm) the spectra may be assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$; also the spectra for Co^{2+} complex show a shoulder strong band

at λ_{\max} (605 nm); this band is due to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, which is attributed in both cases to an octahedral field.

Infrared spectra

The infrared spectra of the solid ligand, the Cu^{2+} , Ni^{2+} and Co^{2+} complexes are discussed at several interest areas of the spectrum, excluding the bonding of the ligand to the metal ions, Table-3.

TABLE-3
SOME IMPORTANT INFRARED SPECTRAL BANDS (cm^{-1}) OF DHBH
AND METAL COMPLEXES

DHBH	Cu^{2+} -DHB	Ni^{2+} -DHB	Co^{2+} -DHB	Assignments
3525 s	3525 m	3525 m	3540 m	$\nu(\text{OH})$
—	—	3410 sbb	3995 sbb	$\nu(\text{H}_2\text{O})$
3170 s	3110 m	—	—	$\nu(\text{N—H})$
1695 s	990 s	1690 m	1695 s	$\nu(\text{C=O})$
1580 s	1555 m	1540 m	1515 m	$\nu(\text{N—H})$
1370 s	1365 s	1365 s	1360 s	$\nu(\text{NO}_2)$
1300 s	1270 m	1265 m	1265 m	$\nu(\text{C—N})$
1205 s	1175 m	1150 m	1135 m	$\nu(\text{C—O})$
—	570 m	560 m	545 m	$\nu(\text{M—O})$
—	445 m	435 m	425 m	$\nu(\text{M—N})$

s = strong, m = medium, bb = broad band

(a) The IR spectra of the ligand show two strong bands at 3565 and 3170 cm^{-1} assignable to $\nu(\text{OH})^{19}$ and $\nu(\text{NH})^{20}$ groups respectively. In case of Cu^{2+} complex, these two groups shifts to lower frequencies, which indicate the sharing of oxygen of hydroxyl group and nitrogen of —NH— in coordination process. Also, the same result occurs in Ni^{2+} and Co^{2+} complexes, but the presence of water molecules coordinated to nickel and cobalt atoms in the complexes renders it difficult to draw conclusion in the $[\text{NH}]$ region of spectra.

(b) The absorption of $\nu(\text{C=O})$ group of free ligand at 1695 cm^{-1} shows a little shift in the solid complexes, which indicates that $\nu(\text{C=O})$ did not play any role in the complexation process: This conclusion is also observed for the NO_2 group as seen from Table-3.

(c) The band at 1580 cm^{-1} of the free ligand, shifted to lower frequencies in all solid complexes, which confirms the sharing of lone pair of nitrogen atom in the complexation process.

(d) Also, two strong bands appear in the free ligand at 1300 and 1205 cm^{-1} which are referred to $\nu(\text{C—N})$ and $\nu(\text{C—O})$ respectively, shifting to lower frequencies, which indicates that the oxygen of —OH groups and the nitrogen atoms are two important sites of donation process.

(e) The very interesting area in the spectra is the appearance of new bands at

lower frequencies due to metal-nitrogen $\nu(\text{M—N})$ and metal-oxygen $\nu(\text{M—O})$ interaction²⁰.

On plotting the frequencies of $\nu(\text{M—O})$ and $\nu(\text{M—N})$ as a function of atomic number of the metals, the results are similar in shape to that obtained by Irving and Williams²¹.

Finally, the results of elemental analysis and the molar conductance are given in Table-4. The values of the molar conductance (10^{-3} M) of solid complex in DMF indicate the non-electrolytic nature of the complexes. Also, the magnetic moment measurements after correction are presented in Table-4, where they equal 1.8, 2.7 and 3.8 B.M. for Cu^{2+} , Ni^{2+} and Co^{2+} complexes respectively. This indicates the presence of one, two and three unpaired electrons for copper, nickel and cobalt complexes respectively. Both magnetic moment and spectral data indicate the square planar geometry for copper and octahedral geometry for both nickel and cobalt complexes.

TABLE-4
ANALYTICAL, MAGNETIC AND CONDUCTANCE DATA FOR
 M^{2+} -DHB COMPLEXES

Compounds	% Analysis calcd. (found)				Conductance $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$	μ_{eff} (B.M.)
	C	H	N	M		
DHBH	51.49 (52.01)	2.97 (2.68)	13.86 (13.44)	—	—	—
$\text{Cu}(\text{DHB})_2$	46.74 (47.23)	2.40 (2.28)	12.58 (13.58)	9.51 (9.39)	11.35	1.8
$\text{Ni}(\text{DHB})_2(\text{H}_2\text{O})_2$	44.65 (45.01)	2.86 (2.40)	12.02 (11.91)	8.43 (8.30)	8.95	2.7
$\text{Co}(\text{DHB})_2(\text{H}_2\text{O})$	45.82 (45.10)	2.64 (2.48)	12.34 (12.61)	8.68 (8.59)	7.42	3.8

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