TABLE 1 — FORMATION CONSTANTS OF RARE-EARTH METAL COMPLEXES OF THE SCHIFF BASE (I)

[Ionic strength = $0.1M$ (NaClO$_4$); temp. = $25°C$; medium = 50% (v/v) (aq. dioxane]

	Least squares[3b]	Correction term[3b]	Block & McIntyre[7]	Standard deviation[3b]
		Sm(III)		
log K_1	7.45	7.42	7.43	
log K_2	6.91	6.92	6.92	
log β_2	14.36	14.34	14.35	±0.03
		Dy(III)		
log K_1	7.06	7.08	7.07	
log K_2	6.88	6.87	6.87	
log β_2	13.94	13.95	13.94	±0.02
		Gd(III)		
log K_1	7.43	7.41	7.40	
log K_2	6.46	6.48	6.49	
log β_2	13.89	13.89	13.89	±0.03
		Pr(III)		
log K_1	7.32	7.32	7.29	
log K_2	6.51	6.52	6.53	
log β_2	13.83	13.84	13.82	±0.04
		Nd (III)		
log K_1	7.03	7.05	7.03	
log K_2	6.46	6.47	6.47	
log β_2	13.49	13.52	13.50	±0.04

between two successive formation constants of the complexes, as revealed by formation curves is less than one log unit and hence the values of log K_1 and log K_2 were evaluated by refined methods of computation[3b,7] and the values are given in Table 1 alongwith standard deviation. The standard deviation for the proton-ligand system was ± 0.04.

The order of formation constants (log β_2) for the trivalent metal chelates is Sm(III) > Dy(III) > Gd(III) > Pr(III) > Nd(III). The non-linear plot of Z^2/r versus log β_2 of these complexes violates the Born relation suggesting that the bond is not predominantly ionic, in confirmity with the earlier observations[8,9].

The degree of formation (α) of each species as a function of free [ligand] or pH was calculated using the expressions (1-3).

$$\alpha_{M(III)} = \frac{1}{1 + \beta_1 [L] + \beta_2 [L]^2} \quad ..(1)$$

$$\alpha_{ML} = \frac{\beta_1 [L]}{1 + \beta_1 [L] + \beta_2 [L]^2} \quad ..(2)$$

$$\alpha_{ML_2} = \frac{\beta_2 [L]^2}{1 + \beta_1 [L] + \beta_2 [L]^2} \quad ..(3)$$

The same were graphically represented as distribution diagrams which give an idea of the formation of different species in significant proportions in solution. As a typical case the distribution curves for Dy(III) system are given in Fig. 1. Similar results were obtained for other systems.
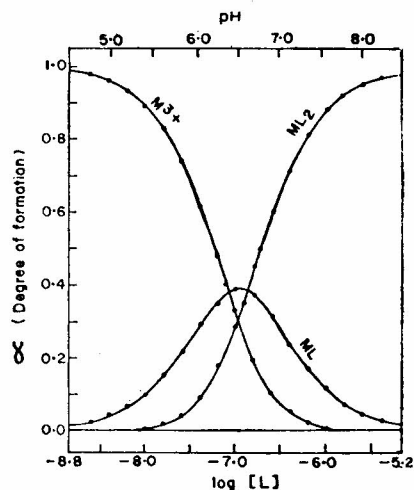

Fig. 1 — Distribution diagram for Dy(III) system.

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Equilibria for Interaction between Hematoxylin & Iron(III), Cobalt(II), Nickel(II) & Copper(II)

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The interactions between hematoxylin and Fe(III), Co(II), Ni(II) and Cu(II) have been investigated potentiometrically and spectrophotometrically. The pH dependence acid-base equilibria of the free ligand has been explained. The pK's of the complex species have been calculated.

HEMATOXYLIN has been widely used for the determination of a number of metal ions[1-6] and in the field of histological studies as a stain[7] for demonstrating the biological activities of different compounds. We therefore thought it important

to study the complex formation equilibria between hematoxylin and Fe(III), Co(II), Ni(II) and Cu(II) employing potentiometric and spectrophotometric methods. To the best of our knowledge this study is the first of its kind undertaken with this important ligand.

Hematoxylin, $C_{16}H_{14}O_6.3H_2O$ (Fluka, AG, Switzerland) was used without purification. A freshly prepared solution was used in each experiment to avoid the probable formation of hematin which is the oxidised product of hematoxylin.

The exact concentrations of Fe(III), Co(II), Ni(II) and Cu(II) were determined as usual[8].

The pH titrations of $10^{-3}M$ of the dried ligand versus standard CO_2-free 10^{-2} M NaOH in the presence of 0.1 M KCl as a supporting electrolyte were carried out employing a Beckman model 4500 digital pH meter, which was standardized as described before[9]. The pK's of the reagent were evaluated. Similar titrations were carried out to evaluate the B-values of the metal ligand systems[9]. The experimental data yielded normal formation curves. Some experiments were done in the aquo-organic solvent containing purified 80% DMSO-20% H_2O mixture (wt/wt)[10]. The glass electrode was soaked in the mixed solvent for 15-20 min before use. This mixed solvent has good solvating ability, high dielectric permeability ($\sim$65), insignificant hygroscopicity and the conventional glass electrode has a Nerstian pH response to give reliable measurements[11]. The solution electronic spectra were recorded on a Unicam SP 1800 instrument.

Electronic spectra of the free ligand — The aqueous solution of the free ligand having pH of 5.77 is yellow in colour. At pH 5.67, the colour changes to mouve and finally the aqueous solution attains blue colour at neutral pH. In alkaline pH the colour is violet, indicating that this compound is highly sensitive to pH of the medium. The position of the visible absorption bands is greatly influenced by pH (Fig. 1), indicating the presence of different absorbing species. The band with λ_{max} at 450 nm in the pH range 1.25-5.00 undergoes a regular bathochromic shift on increasing the pH as a result of proton elimination. In neutral solutions two bands are traced with λ_{max} at 450 nm and 565 nm. On increasing the pH, the 450 nm band is steadily depressed, while the 565 nm band becomes more intense due to the formation of a quinonoid structure (pH > 7.36). The isosbestic point at 490 nm is due to the equilibrium between the neutral and monoionized species whereas that located at 500 nm is for the equilibrium between the latter species and the divalent anion. The absorbance-pH profile suggests different acid-base equilibria in solution. The curves showing maxima at 450 and 565 nm also exhibit two inflections due to the equilibrium between different ionic species. The lower part of the absorbance-pH curve indicates the equilibrium between the protonated (the lone pair of electrons on the ethereal linkage) and the neutral forms of the compound. This suggests that the predominant form in acid solution is the cationic species, which undergoes deprotonation giving the neutral form with increasing pH. In the compound under investigation with a general symbol H_5L, the free hydroxyl group is firstly ionized giving the first pK_1. The symmetrical o,ō-hydroxy groups associated through the intramolecular hydrogen bond are subjected to further ionization to give rise to pK_2 value. So, the electronic structure is more or less delocalized through resonance interaction. Figure 2 represents the mode of ionization on changing [H+]. The pKs values were calculated using different methods of calculations based on absorbance-pH relationship, namely : half-height[12], limiting absorption[13] and Colleter[14]. The results are collected in Table 1, with an average pK_1 and pK_2 values of 3.82 ± 0.05 and 6.88 ±
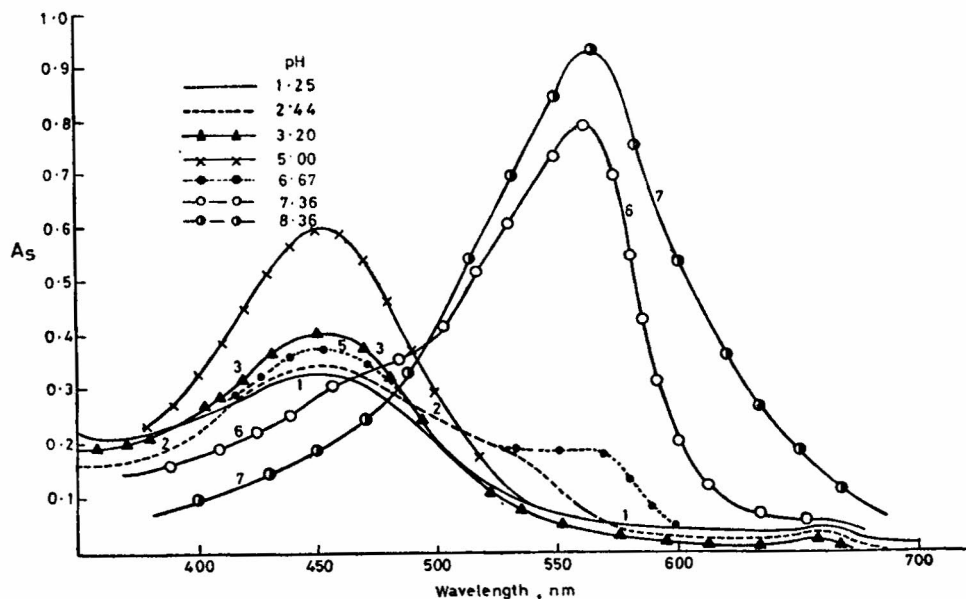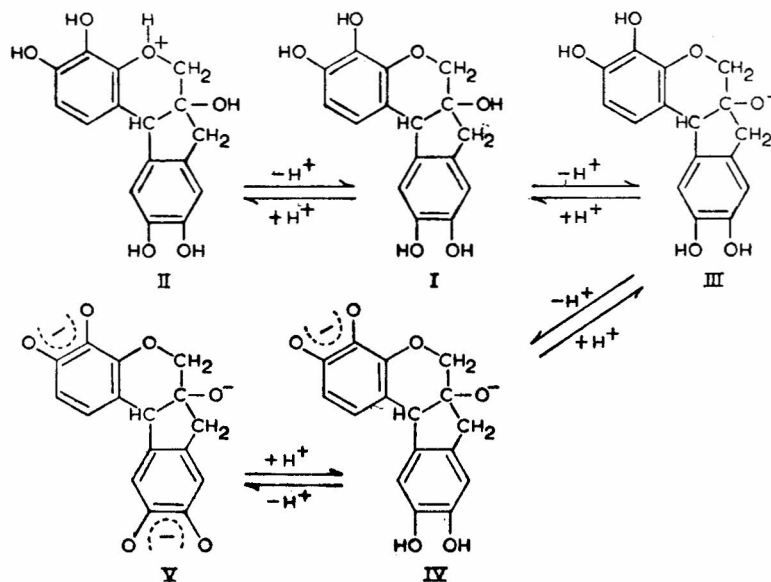

Fig. 1 — Effect of pH on electronic absorption spectrum of of 2×10^{-4} M solution of hematoxylin

Fig. 2 — Mode of ionization of hematoxylin at different pH values

0.05 respectively. This indicates that two protons are ionized from this compound inspite of the existence of five protons. This was further verified by plotting of pH versus log absorbance ratio[13]. The slope value for such a linear plot came out to be 1.86.

Potentiometric studies of the free ligand and its complexes — The formation curve of the ligand was constructed by plotting the $\bar{n}_A$ (the number of protons attached to the reagent) versus pH of the solution corresponding to each addition of alkali. The ligand yielded a maximum $\bar{n}_A$ value of 2, indicating that hematoxylin behaves as a dibasic acid. The formation curves for the metal complexes were constructed by plotting $\bar{n}$ against pL. Basic equations related to stepwise complex equilibria were derived. Special attention was paid to the determination of the stability constants. A description of the mathematical methods used for this purpose and a large body of data on the stability constants of metal complexes are found in various reviews and monographs[15,16]. The stabilities (Table 1) of the presently studied complexes follow Irving and William order, with the exception of cobalt system. The anomalous behaviour of cobalt system may be attributed to the oxidation of cobalt(II) to cobalt (III). This was supported by the fact that for cobalt system when $\bar{n} > 1$ the pH meter readings showed a tendency to drift back to more acid values. This could be related to the delocalization among π-orbitals in the benzene ring and p-orbitals of the coordinating oxygen atoms and the d-orbitals of the transition metal atom, with the expectation to be members of electron-transfer series[17]. The pK's for all the studied systems in aqueous DMSO are higher than in aqueous media by ~3 units. This is related to the solvating property of the solvent, DMSO.

TABLE 1 — pK VALUES OF HEMATOXYLIN(L) AND ITS COMPLEXES

Compound	Potentiometry		Spectrophotometry	
	H_2O	80% DMSO 20% H_2O	H_2O	80% DMSO 20% H_2O
L	7.12 ± 0.02	9.44 ± 0.02	3.82 ± 0.05 6.88 ± 0.05	9.25 ± 0.12
FeL	3.54 ± 0.04	5.94 ± 0.06	3.38 ± 0.04	6.41 ± 0.05
CoL	6.34 ± 0.04	9.68 ± 0.02	6.30 ± 0.05	9.62 ± 0.04
Nil	7.42 ± 0.02	9.92 ± 0.04	7.25 ± 0.04	9.84 ± 0.05
CuL	5.86 ± 0.12	8.74 ± 0.06	5.91 ± 0.05	8.92 ± 0.04

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Spectrophotometric Determination of Molybdenum by Extraction of its Thiocyanate Complex into Chloroform

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A simple, rapid, selective and sensitive method for the spectrophotometric determination of molybdenum at microgram level has been developed by extracting Mo(V)-thiocyanate complex into chloroform from ethanolic solution. It has a Beer's law range of 0-5 μg Mo/ml with Sandell's sensitivity of 0.014 μg Mo/cm². W(VI) Cr(VI), V(V), Fe(III), Cu(II), Ni(II), Co(II) and Pd(II) do not interfere. The method has been used to estimate Mo in various synthetic samples.

THE oftenly used colour reaction between molybdenum and thiocyanate in the presence of a reducing agent, still forms the basis of determination of microgram quantities of the element colorimetrically despite its several limitations arising out of co-extraction of other elements under different conditions. We present here a modified method for the estimation of molybdenum using the same reaction but extracting the molybdenum thiocyanate complex into chloroform. The proposed method enhances considerably the selectivity and has high sensitivity.

A stock solution of molybdenum containing 10 mg Mo/ml was prepared by dissolving sodium molybdate dihydrate (E. Merck) in distilled water. The solution was standardised gravimetrically by the oxine method[1]. Working solutions at the μg/ml level were prepared by suitable dilutions. Solutions of other metal ions (mg/ml) were prepared using their C. P. grade salts.

Aqueous solutions of ferrous ammonium sulphate (1% in 0.2N H_2SO_4) and ammonium thiocyanate (20%) were prepared. Solution of stannous chloride (20%) was prepared by heating to dissolve its dihydrate in 20 ml HCl (1:1) and diluting it to 100 ml after cooling.

Chloroform and ethyl alcohol were distilled before use.

Procedure — To the solution containing 100 μg molybdenum in a 100-ml separatory funnel, were added 1.2 ml hydrochloric acid (10 M), 1 ml ferrous solution (1%), 1 ml ammonium thiocyanate (20%), 1 ml freshly prepared stannous chloride (20%) and 10 ml ethyl alcohol. The final volume was made upto 20 ml by adding water. It was mixed and equilibrated once with an equal volume of chloroform for one min. The solvent layer was filtered through a filter paper No. 41 (free from iron) to remove hanging droplets of water (if any), volume made upto 25 ml in a volumetric flask with chloroform and the absorbance was measured with a 'Spekker Absorptiometer' (Hilger and Watts) using Kodak filter No. 2 (465 nm) and 1 cm cells against a reagent blank prepared similarly.

In acid media, molybdenum is reduced by stannous chloride to pentavalent state and it forms an orange complex with thiocyanate. The coloured species is quantitatively extracted into chloroform in the presence of ethyl alcohol and its absorbance is influenced by change in operative parameters as indicated below.

The absorbance is 0.145 at 0.6M HCl if the solution contains 100 μg Mo, 1 ml ferrous solution (1%), 1.5 ml ammonium thiocyanate (20%), 1.5 ml stannous chloride (20%), 5 ml ethyl alcohol in a final volume of 20 ml. In the acid range 0.5-0.8M HCl, the absorbance is constant. Further increase in acidity (>0.8M) lowers the absorbance value. In the absence of ethyl alcohol, the molybdenum thiocyanate complex is not at all extracted into chloroform. Alcohol being the basis of extraction, the absorbance is only 0.085 if 0.6M HCl solution contains 4 ml of it and reaches a maximum value of 0.295 for 10-11 ml of ethanol. If the aqueous solution contains 0.2 ml of ferrous solution, the absorbance of Mo(V)-thiocyanate is only 0.11; but it increases with the increase in [Fe(II)] and has a maximum value of 0.295 for 1-1.5 ml of Fe(II). Higher amounts of iron require correspondingly higher amounts of stannous chloride. The absorbance shows an upward trend with the increasing concentration of thiocyanate. It is 0.145 if the solution contains 0.2 ml thiocyanate, increases to 0.21 with 0.5 ml thiocyanate and then remains constant at 0.295 for 1.0-3.0 ml of the thiocyanate reagent. The Mo(V)-thiocyanate has the maximum absorbance if the solution contains 1.0-3.0 ml of stannous chloride (20%).

Consideration of the above data has led to the finalization of the following optimum conditions for Mo upto 125 μg : 0.6 M HCl, 1 ml Fe(II) solution (1%), 1 ml NH_4SCN (20%), 1 ml $SnCl_2.2H_2O$ (20%), 10 ml ethyl alcohol in a total volume of 20 ml, equilibrating once for 1 min with an equal volume of chloroform. The Mo(V) complex is stable for ~90 min with absorbance maxima at 465 nm.

Sulphate, chloride, acetate, citrate, nitrate, fluoride, tartrate and phosphate (> 10) (figures in parentheses are amounts in mg/ml) do not affect the absorbance while oxalate (0.5) lowers it slightly. W(VI) (1.5), Cr(VI) (1.5), U(VI) (1.5), V(V), (2.5), Fe(III) (0.05), Cu(II) (5), Ni(II) (5), Co(II) (0.05), Mn(II) (5), Pd(II) (0.05) do not influence the estimation. Re(VII) interferes.

The Mo(V) complex with thiocyanate showed molar absorptivity of 7074 litre mol⁻¹ cm⁻¹, corresponding to Sandell's sensitivity of 0.014 μg/cm². The Beer's law is obeyed in the range 0—5 μg of Mo/ml. The proposed method compares favourably with other thiocyanate methods (Table 1).