

**THERMODYNAMICS, STABILITY CONSTANTS  
AND SPECTROPHOTOMETRIC STUDIES OF COMPLEXES  
OF TRIVALENT LANTHANIDES AND SOME DIVALENT METALS  
WITH 3-[ $\alpha$ -(*o*-HYDROXYPHENYL)ETHYLIDENEHYDRAZINO]-  
6-PHENYLPYRIDAZINE LIGAND**

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**ABSTRACT**

The stepwise stability constants of trivalent lanthanide metal ions with 3-[ $\alpha$ -(*o*-hydroxyphenyl)ethylidenehydrazino]-6-phenylpyridazine (*o*-OHAHPP) have been determined by pH-metric titration. The stepwise stability constants of complexes of Cu(II), Ni(II), Co(II), Zn(II) and  $\text{UO}_2^{2+}$  ions with the *o*-OHAHPP ligand have also been measured. The relative stabilities of the 1:1 metal-*o*-OHAHPP complexes of the transition metal ions were found to be  $\text{UO}_2(\text{II}) < \text{Cu}(\text{II}) > \text{Ni}(\text{II}) > \text{Co}(\text{II}) > \text{Zn}(\text{II})$ .

The effect of temperature (at 10, 20, 30 and 40°C) has also been examined for selected rare earth (Pr(III), Sm(III), Gd(III), Dy(III) and Yb(III)) *o*-OHAHPP complexes. The overall changes in  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  have been calculated. Negative values of  $\Delta H$  were obtained, indicating that the complexation reactions are exothermic. Since the values of both  $\log K_1$  and  $\log \beta$  decrease with increasing temperature, the complex formation reaction is not favoured by increasing temperature. The  $\Delta G$  values are negative for all the chelates, indicating that these reactions are spontaneous. The  $\Delta S$  values are positive for all the chelates, indicating that entropy considerations favour complex formation.

Spectrophotometric studies have been performed on solutions of Cu(II) and Co(II) with *o*-OHAHPP of varying pH. The optimum pH for complex formation is 6.0 for both Cu(II) and Co(II) *o*-OHAHPP complexes. The compositions of the chelates formed have been determined by various methods. A 1:1 metal-ligand ratio was observed in the case of Cu(II), and 1:1 and 1:2 ratios in the case of Co(II)-*o*-OHAHPP.

**INTRODUCTION**

Pyridazine(1,2-diazine) and its benzo analogues have been known since the nineteenth century, but early interest in these compounds was not very intense as they were not found in nature. However, during the last three decades intensive research has been stimulated because many derivatives have found applications as a result of their biological activity, and some are used as drugs [1]. Moreover, it is known that the antiviral activities of the

complexes are more potent than the free ligands [2]. These facts have stimulated our interest in the synthesis of metal complexes of pyridazines which may find applications in biological chemistry. We report here on studies of the behaviour of complexes of some transition and lanthanide elements with ligands containing the pyridazine moiety. The effect of pH, composition and the stability of Cu(II) and Co(II) complexes were determined spectrophotometrically. Stepwise stability constants and the thermodynamic parameters  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  were calculated for Ni(II) and five selected lanthanide ions in a 75% (v/v) dioxane–water system.

## EXPERIMENTAL

### *Synthesis of the organic ligands*

The organic ligands under investigation were synthesized by condensing the parent compound 3-hydrazino-6-phenylpyridazine [3] (HPP) with benzil [4], *p*-methoxyacetophenone, and *o*-hydroxyacetophenone to obtain the corresponding Schiff base derivatives BHPP *p*-MeOAHPP and *o*-OHAHPP respectively (see Table 1).

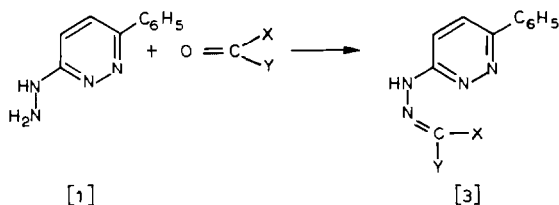


TABLE 1

Schiff base derivatives

Derivative	X	Y	Description	m.p. (°C)
<b>3a</b> BHPP	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> -C=O	Yellow crystals	170 [4]
<b>3b</b> <i>p</i> -MeOAHPP	CH <sub>3</sub>	C <sub>6</sub> H <sub>4</sub> -OCH <sub>3</sub> ( <i>p</i> )	Pale yellow crystals	188 [4]
<b>3c</b> <i>o</i> -OHAHPP	CH <sub>3</sub>	C <sub>6</sub> H <sub>4</sub> -OH( <i>o</i> )	Yellow crystals	234 (ethanol)

Numbers in square brackets denote references.

Analysis of **3c** gave the following results. Calc.: C 71.05%; H 5.26%; N 18.42%. Found: C 71.30%; H 5.10%; N 18.40%. The IR spectrum showed a broad band at 3500 cm<sup>-1</sup>  $\nu$ (OH),  $\nu$ NH stretch at 3150 cm<sup>-1</sup> and  $\nu$ C=N stretch at 1620 cm<sup>-1</sup>.

### *Reagents and materials*

Stock solutions of the lanthanide nitrates were prepared from their oxides (BDH) and standardized as described previously [5]. Solutions of the metal

nitrate salts were prepared and standardized using EDTA in the presence of suitable indicators [6]. Dioxane was purified as described previously [4]. Universal buffer and potassium hydroxide were prepared and standardized by the recommended methods [6]. All other chemicals used were of reagent grade.

### *Measurements and procedures*

The pH-metric titrations and all other experimental conditions were essentially the same as described previously [4,7]. The temperature was maintained at 30 °C and the ionic strength at 0.05 M using KNO<sub>3</sub>. All measurements were taken in 75% (v/v) dioxane–water solution. The stability constants of Cu(II)–, Ni(II)–, Co(II)–, Zn(II)–, UO<sub>2</sub>(II)– and lanthanide Ln(III)–*o*-OHAHPP chelates were determined at 30 °C. The stability constants of Ni(II)–, Pr(III)–, Sm(III)–, Gd(III)–, Dy(III)– and Yb(III)–*o*-OHAHPP chelates were determined at various temperatures (10, 20, 30 and 40 °C), to allow calculation of the thermodynamic constants  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  for the chelating reactions. The values of the hydrogen ion concentrations were corrected by adding a correction factor of 0.28 pH unit [8]. The pH measurements, and calculation of the stability constants and thermodynamic functions were performed as described previously [4,7].

The electronic absorption spectra of the chelate compounds were recorded using a Perkin–Elmer 550 S spectrophotometer with the ligand solution as a reference in a 50% (v/v) dioxane–water mixture. The pH-metric titrations were carried out using a WTW digital pH meter 520 fitted with a combined electrode.

## RESULTS AND DISCUSSION

### *pH-metric studies*

#### *Dissociation constant of the organic ligands*

The proton–ligand dissociation constants ( $pK^H$ ) were determined for the ligands in 75% (v/v) dioxane–water solvent (Table 2). The  $pK^H$  values for the ligands studied were found to be 13.08, 13.25, 12.62 and 12.48 for HPP, *p*-MeOAHPP, BHPP and *o*-OHAHPP, respectively. These  $pK^H$  values appear to be affected by the structures of the various ligands. The *p*-MeOAHPP ligand has the highest value of  $pK^H$  (13.25), which can be attributed to the increase of electron density on the hydrazone moiety by the electron-repelling property of the methoxy group, which retards the removing of the ligand proton and increases its basicity. In the case of the BHPP and *o*-OHAHPP ligands, however, the presence of electron-withdrawing groups (i.e. carbonyl and hydroxyl groups) decreases the electron density on

TABLE 2

Stability constants of 1:1 and 1:2 divalent metal ions with X-3-hydrazino-6-phenylpyridazine ligands in 75% (v/v) dioxane–water at 30 °C and  $\mu = 0.05$  M KNO<sub>3</sub>

Cation	X = H <sub>2</sub> (parent) (HPP) <sup>a</sup>		X = <i>p</i> -methoxy- acetophenone ( <i>p</i> -MeOHAPP) <sup>a</sup>		X = benzil (BHPP) <sup>a</sup>		X = <i>o</i> -hydroxy- acetophenone ( <i>o</i> -OHAHPP)	
	log <i>K</i> <sub>1</sub>	log β	log <i>K</i> <sub>1</sub>	log β	log <i>K</i> <sub>1</sub>	log β	log <i>K</i> <sub>1</sub>	log β
p <i>K</i> <sup>H</sup>	13.08	–	13.25	–	12.62	–	12.48	–
Co <sup>2+</sup>	8.58	16.88	8.74	17.19	10.60	19.00	11.92	22.56
Ni <sup>2+</sup>	8.28	16.37	8.54	16.84	11.33	19.66	11.85	↓↓
Cu <sup>2+</sup>	12.15	–	12.51	19.92	12.00	22.27	12.35	22.05
Zn <sup>2+</sup>	8.01	15.68	8.47	16.94	9.15	–	10.19	↓↓
Cd <sup>2+</sup>	↓↓	–	7.17	14.08	8.00	–	–	–
UO <sub>2</sub> <sup>2+</sup>	11.02	↓↓	11.47	↓↓	11.30	22.30	11.95	↓↓

<sup>a</sup> Ref. 7.

the hydrazone moiety, and its proton is easily removed. Thus, the basicity of the complexing agents BHPP and *o*-OHAHPP are decreased while the basicity of the *p*-MeOAHPP ligand is increased compared with the parent ligand (HPP). The complexing agents are ordered by basicity (i.e. p*K*<sup>H</sup> values) as follows: *p*-MeOAHPP > HPP > BHPP > *o*-OHAHPP. The *o*-OHAHPP ligand behaves as a weakly monoprotic compound, with the p*K*<sup>H</sup> (value (12.48) indicating that the proton produced is attributable to the hydrazone moiety. This behaviour is similar to that observed by Holst [9] for the *o*-hydroxybenzoylacetone (*o*-OHBA) ligand: he found that the *o*-OHBA ligand behaves as a monoprotic ligand, and that its p*K*<sup>H</sup> value is nearly the same as that for benzoylacetone itself.

#### *Stability constants of transition metal chelate compounds*

Representative plots of the titration curves of the *o*-OHAHPP ligand in the absence and in the presence of divalent metal ions (Cu(II), Ni(II), Co(II), Zn(II)) and UO<sub>2</sub><sup>2+</sup> ions are shown in Fig. 1. The titration curve of *o*-OHAHPP (3 × 10<sup>-3</sup> M) in the presence of Cu(II) (1.5 × 10<sup>-3</sup> M) showed distinct inflections at *m* = 1 and 2 (*m* = number of moles of base added per mole of metal ion), indicating the stepwise formation of ML and ML<sub>2</sub> complexes, respectively (Fig. 1). However, a different behaviour was observed in titration curves of the *o*-OHAHPP ligand in the presence of other metal ions. In the presence of Co(II) ions, a weak inflection at *m* = 1 was followed by a sharp inflection at *m* = 2, indicating the formation of ML and ML<sub>2</sub> species (Fig. 2). In addition, a third buffer zone was observed between pH values 7.0 and 8.5, accompanied by a sharp inflection. This may be due to the formation of hydroxo complexes (ML<sub>2</sub>OH). The possibility of the formation of metal hydroxide is excluded, since no precipitate was observed

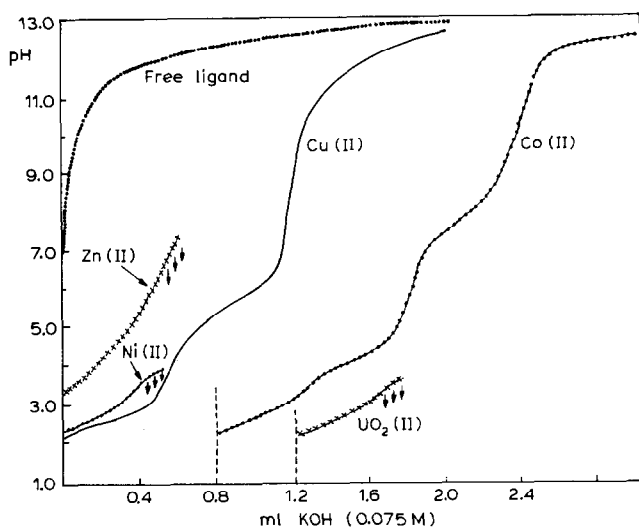


Fig. 1. pH titration curves of the *o*-OHAHPP ligand and its metal complexes at 30 °C in a 75% (v/v) dioxane–water mixture:  $[L] = 3 \times 10^{-3}$  M (free ligand),  $[Metal] = 1.5 \times 10^{-3}$  M,  $V_0 = 30$  ml,  $\mu = 0.05$  M ( $KNO_3$ ).

in the titration cell. In the case of Ni(II), Zn(II) and  $UO_2^{2+}$  ions with *o*-OHAHPP the titrations could not be completed, owing to the appearance of precipitates. For this reason, only the values of  $\log K_1$  have been

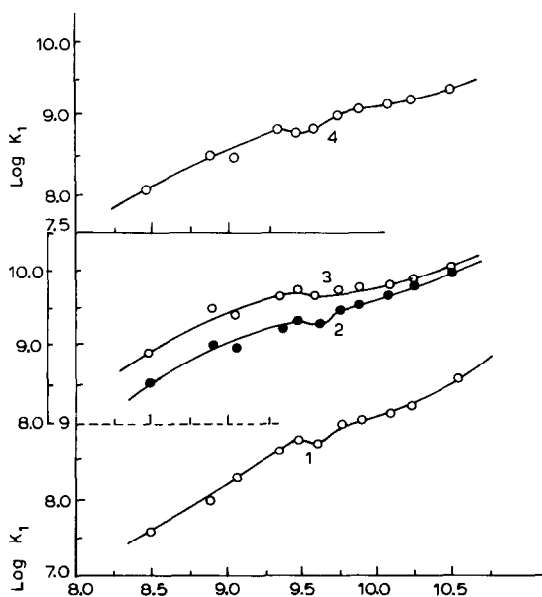


Fig. 2.  $\log K_1$  as a function of ionic potential  $Z^2/r$  for lanthanide(III) complexes at 30 °C,  $\mu = 0.05$  M, in 75% (v/v) dioxane–water mixtures. 1, Ln(III)–*o*-OHAHPP; 2, Ln(III)–*p*-MeOAHPP; 3, Ln(III)–HPP; 4, Ln(III)–BHPP.

calculated for the Ni(II), Zn(II) and  $\text{UO}_2^{2+}$  chelates. For the Cu(II) and Co(II) chelates, both  $\log K_1$  and  $\log K_2$  values could be evaluated. In the case of Cd(II) no stability constants could be evaluated, as a precipitate was observed at the beginning of titration.

The complex formation reactions and their compositions and structures depend on the metal ion, the nature of the ligand and the medium of the reaction. The charge and radius of the ion as well as the stabilization owing to orbital splitting play an important role in the stabilization of complexes [10]. The stability of oxygenated cation complexes ( $\text{UO}_2^{2+}$ ) is fairly high [11]. This is attributable to the bonded oxygen atoms increasing the electrostatic attraction between the metal ion and the coordinated ligands, and overcoming any steric hindrance offered by the oxygenated cation.

The order of increasing stability constants for metals with the *o*-OHAHPP ligand is in good agreement with the order found previously for other related complexing agents [4,7], i.e.  $\text{Zn(II)} < \text{Cu(II)} > \text{Co(II)} > \text{Ni(II)}$ , except for the BHPP ligand, with which Co(II) and Ni(II) exchange positions in the order. Two important factors affecting the stability of the complexes formed are the basicity and the structure of the ligand. The high stability constant values characterizing the *ortho* substituted ligands (i.e. *o*-OHAHPP and BHPP [7]) compared with those of other related ligands (HPP [7] and *p*-MeOAHPP [7]) indicate that the structure effect overcomes the basicity effect. A comparison of the  $\log K_1$  values of the various ligand chelates (Table 2) reveals the following order of stability: *o*-OHAHPP > BHPP > *p*-MeOAHPP > HPP.

#### *Stability constants of Ln(III) chelate compounds*

The molar ratio of metal to ligand was kept constant at 1 : 2. The titration curves of the metal–ligand mixtures differ in shape and are separated by depression in pH value from that of the free ligand, confirming the complexation process [4]. With metal–ligand ratios of 1 : 2, and in some cases 1 : 3 and 1 : 5, there is only one sharp inflection at  $m = 2$  ( $m$  = number of moles of KOH added per mole of metal) [4], confirming that complexes of ratio 1 : 2 are predominant. The relationship between the stability constants ( $\log K_1$ ) of the lanthanide complexes and the ionic potentials ( $Z^2/r$ ) of the lanthanide ions is shown in Fig. 2. Instead of the expected linearity attributable to electrostatic interaction, curves were obtained showing a gradual increase in stability between La(III) and Eu(III), followed by a small decrease in the Gd(III) region (Fig. 2). The same behaviour has been observed before for a variety of chelating agents [4,12–15]. Some authors have attributed this deviation from linearity beyond gadolinium to changes in hydration along the cation series [16–18]. The similarity of the behaviour of the ligand studied here to that of other related ligands [4,12,13] is due to the presence of similar coordinating sites in the ligands. The overall stability constants  $\beta$  for lanthanide chelates of *o*-OHAHPP compared with ligands of

TABLE 3

Stability constants of 1:1 and 1:2 trivalent lanthanide metal ions with X-3-hydrazino-6-phenylpyridazine ligands in 75% (v/v) dioxane-water at 30 °C ± 0.05 and  $\mu = 0.05$  M (KNO<sub>3</sub>)

Ln(III) cation	X = benzil (BHPP) <sup>a</sup>		X = <i>p</i> -methoxy- acetophenone ( <i>p</i> -MeOAHPP) <sup>a</sup>		X = <i>o</i> -hydroxy- acetophenone ( <i>o</i> -OHAHPP)		X = H <sub>2</sub> (parent HPP) <sup>a</sup>	
	log K <sub>1</sub>	log β	log K <sub>1</sub>	log β	log K <sub>1</sub>	log β	log K <sub>3</sub>	log β
pK <sup>H</sup>	12.62	–	13.25	–	12.48	–	13.08	–
La	8.05	16.28	8.55	17.20	7.60	15.45	8.90	17.69
Pr	8.50	17.13	9.12	18.34	8.00	16.15	9.48	18.79
Nd	8.42	17.02	9.02	18.21	8.30	16.85	9.36	18.67
Sm	8.85	17.95	9.27	18.82	8.65	17.55	9.64	19.36
Eu	8.77	17.79	9.41	19.06	8.80	17.82	9.73	19.51
Gd	8.83	17.97	9.36	18.96	8.76	17.82	9.67	19.33
Tb	9.06	18.40	9.61	19.44	9.05	18.35	9.75	19.59
Dy	9.08	18.42	9.62	19.51	9.05	18.28	9.79	19.60
Ho	9.15	18.54	9.78	19.90	9.09	18.39	9.76	19.59
Er	9.18	18.65	9.93	20.16	9.23	18.66	9.79	19.69
Yb	9.36	19.02	10.04	20.40	9.55	19.17	9.94	20.04

<sup>a</sup> Ref. 4.

the same moiety (Table 3) follow the order HPP > *p*-MeOAHPP > BHPP > *o*-OHAHPP, which parallels that of the values of the basicity (pK<sup>H</sup>) of the complexing agents. The slight increase in the stability values of the HPP (parent) chelates (pK<sup>H</sup> = 13.08) relative to those of the *p*-MeOAHPP chelates (pK<sup>H</sup> = 13.25) may be attributable to the difference in size of the chelating ligands [4].

#### *Effect of temperatures and thermodynamic parameters of chelate compounds*

The dissociation constant pK<sup>H</sup> for the *o*-OHAHPP ligand was calculated at various temperatures. The values obtained are given in Table 4. These values indicate that neutralization reactions of this ligand are temperature-dependent. The enthalpy change  $\Delta H_1$  was deduced from Arrhenius plots of pK<sup>H</sup> vs. 1/*T*. The free energy change  $\Delta G_1$  and the entropy change  $\Delta S_1$  were calculated using the relationships

$$\Delta G = -2.303RT \log K_1^H \quad (1)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (2)$$

$$-RT \ln K = \Delta H - T \Delta S \quad (3)$$

The positive values of  $\Delta H_1$  indicate that the neutralization reactions of *o*-OHAHPP are endothermic. The ionization of this ligand is enhanced with increasing temperature. The large positive values of  $\Delta G_1$  indicate that the dissociation of *o*-OHAHPP is not spontaneous, and that a rise in temper-

TABLE 4

Thermodynamic functions and stepwise stability constants for 1 : 1 and 1 : 2 for Ni(II)-*o*-OHAHPP and Ln(III)-*o*-OHAHPP chelates at various temperatures

Cation	Temperature (°C)						$-\Delta G_1$ (kcal mol <sup>-1</sup> )	$-\Delta H_1$ (kcal mol <sup>-1</sup> )	$-\Delta G_2$ (kcal mol <sup>-1</sup> )	$-\Delta H_2$ (kcal mol <sup>-1</sup> )	$\Delta S_1$ (cal mol <sup>-1</sup> deg <sup>-1</sup> )	$\Delta S_2$ (cal mol <sup>-1</sup> deg <sup>-1</sup> )			
	10	20	30	40	log $K_1$	log $K_2$									
	log $K_1$	log $K_2$	log $K_1$	log $K_2$	log $k_1$	log $K_1$	log $K_2$	log $K_1$	log $K_2$						
pK <sup>H</sup>	12.96	-	12.75	-	12.48	-	12.21	-	12.21	-	-17.15	-9.14	-	-26.88	-
Ni <sup>2+</sup>	12.15	-	12.00	-	11.85	-	11.60	-	11.60	-	16.20	9.14	-	23.69	-
Pr <sup>3+</sup>	-	-	8.21	8.37	8.00	8.15	7.71	7.90	7.90	11.03	9.14	11.27	10.66	6.24	2.01
Sm <sup>3+</sup>	-	-	8.76	9.06	8.65	8.90	8.38	8.65	8.65	11.90	9.14	12.27	10.66	9.11	5.31
Gd <sup>3+</sup>	-	-	8.97	9.27	8.76	9.06	8.60	8.87	8.87	12.15	9.14	12.55	10.66	9.93	6.24
Dy <sup>3+</sup>	-	-	9.34	9.56	9.05	9.23	8.95	9.14	9.14	12.61	9.14	12.88	10.66	11.45	7.33
Yb <sup>3+</sup>	-	-	9.70	9.98	9.55	9.62	9.37	9.57	9.57	13.20	9.14	13.46	10.66	13.40	9.24



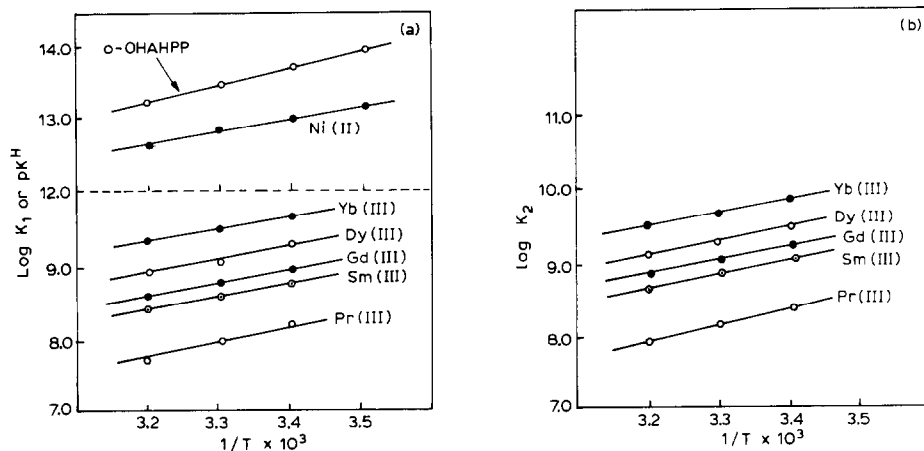


Fig. 3. (a)  $\log K_1^H$  vs.  $1/T$  plots of  $o$ -OHAHPP, and  $\log K_1$  vs.  $1/T$  plots for Ln(III) complexes; (b)  $\log K_2$  vs.  $1/T$  plots for Ln(III) complexes.

ature shifts the equilibrium to the right, i.e. it enhances the dissociation of the ligand.

The stability constants of the complexes decrease with increasing temperature, indicating that complex formation reactions are favoured at low temperatures (Table 4). The stepwise thermodynamic parameters  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the chelate compounds were calculated from the stepwise stability constants obtained at various temperatures (10, 20, 30 and 40 °C) and these are also given in Table 4.  $\Delta H_1$  and  $\Delta H_2$  values of the complexes formed were obtained using Arrhenius plots, as presented in Fig. 3. The large negative values of  $\Delta G_1$  and  $\Delta G_2$  obtained in all cases indicate that the complex formation reactions proceed spontaneously. The value of  $\Delta G_1$  obtained for the Ni(II) chelate is higher than those for the Ln(III) chelates (Table 4), indicating that complex formation for the Ni(II) chelate proceeds more spontaneously than it does for the Ln(III) chelates.

The high negative values of enthalpy changes  $\Delta H_1$  and  $\Delta H_2$  for the 1 : 1 and 1 : 2 lanthanides chelates (Table 4) indicate that the reactions of lanthanides with  $o$ -OHAHPP are exothermic.

The stepwise entropy changes  $\Delta S_1$  and  $\Delta S_2$  for all the lanthanide chelates have positive values indicating that entropy considerations favour complex formation [20]. The value of the entropy change  $\Delta S_1$  for the Ni(II) chelate is higher than the corresponding values for the Ln(III) chelates, indicating that the Ni(II) chelate is favoured.

### Spectrophotometric studies

#### Absorption spectra of metal- $o$ -OHAHPP mixtures

Evidence for complexation was obtained from absorption spectral measurements in 50% (v/v) dioxane-water solutions of these complexes using a

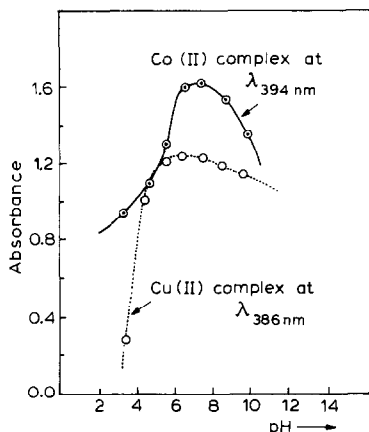


Fig. 4. Absorbance vs. pH for metal chelates at concentrations of  $1.5 \times 10^{-4}$  M *o*-OHAHPP and  $3 \times 10^{-5}$  M metal ion in universal buffer solution using 50% (v/v) dioxane–water (*o*-OHAHPP used as a reference).

solution of the ligand (*o*-OHAHPP) as a reference. On the addition of Cu(II) ions ( $5 \times 10^{-5}$  M) to the ligand solution ( $2 \times 10^{-4}$  M), there developed a greenish yellow colour. In the case of Co(II), the colour was changed from yellow to deep yellow. The absorption spectra of the complexes formed showed strong bands at 388 and 394 nm for Cu(II) and Co(II), respectively.

#### *Effect of pH on the absorption spectra of M(II) complexes*

A spectrophotometric study of the effect of variation of pH on the formation of the various metal chelates with *o*-OHAHPP revealed that Cu(II) and Co(II) form coloured chelates in the pH range 3.0–6.5. The optimum pH range for complex formation was found to be 6.0 for both metal chelates (Fig. 4). However, at pH values higher than 7.5 the absorbance of the Co(II) chelate decreases with increasing pH, which may be attributable to decomposition of the complex.

#### *Validity of Beer's law*

The complexes of Cu(II) and Co(II) with *o*-OHAHPP obeyed Beer's law in the concentration range  $1 \times 10^{-5}$ – $8 \times 10^{-4}$  M (Fig. 5). The molar absorptivity  $\epsilon$  was found to be 18 000 and 31 000  $\text{mol}^{-1} \text{cm}^{-1}$  for the Cu(II) and Co(II) chelates, respectively. The molar absorptivity values obtained for the complexes provide a good sensitive method for the determination of these metal ions.

#### *Composition of the complexes*

The compositions of the Cu(II) and Co(II) metal–ligand systems in solution were determined by the method of continuous variation (Job's method) [21]. Equimolar solutions of ligand and metal ion ( $1.8 \times 10^{-4}$  M)

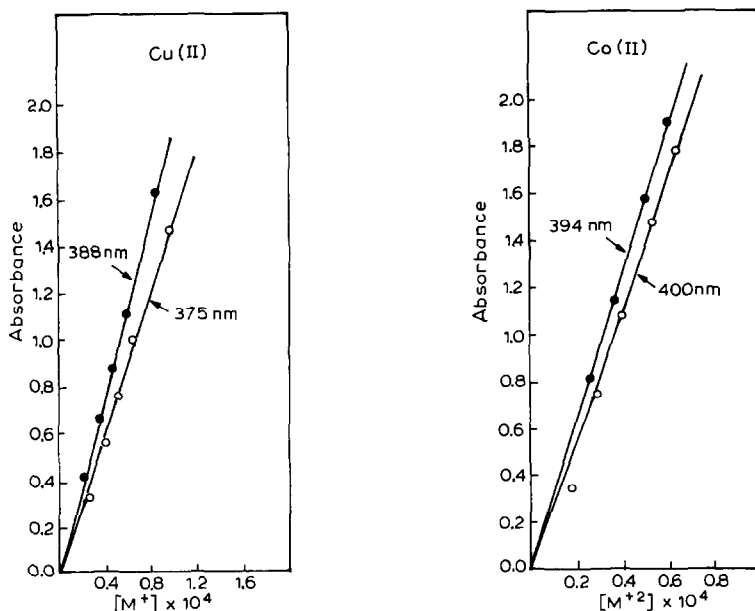


Fig. 5. Validity of Beer's law for  $M^{2+}$ -*o*-OHAHPP complexes.  $[L] = 2 \times 10^{-4}$  M in a 50% dioxane-water mixture at pH 6.0.

were mixed to a volume of 10 ml at the optimum pH (6.0). The Cu(II)-ligand ratio was found to be 1:1 at the various wavelengths measured (Fig. 6a), while the composition of Co(II)-*o*-OHAHPP complexes determined at pH = 6.0 revealed that both 1:1 and 1:2 compositions were present in solution (Fig. 6b). The compositions of the complexes were further confirmed by other methods, e.g. the slope ratio [22] and limiting logarithmic

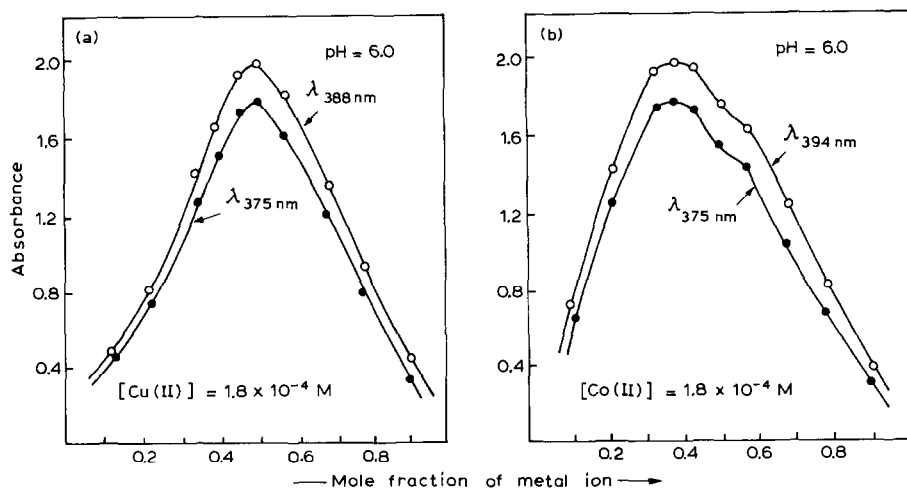


Fig. 6. Job's Method for  $M(II)$ -*o*-OHAHPP complexes in 50% (v/v) dioxane-water.

methods [23]. The results obtained by these means were in good agreement with those obtained by Job's method.

*Spectrophotometric determination of stability constants of metal complexes*

The stability constants of the complexes were determined spectrophotometrically by measuring the absorbance of solutions of the metal–ligand mixture at a fixed concentration but at varying pH (Fig. 4). The spectra of the fully formed complexes were measured. The degree of formation of the complex was obtained using the relationship [24]

$$\bar{n} = \frac{O_{D_x} - O_{D_L}}{O_{D_{ML}} - O_{D_L}} \quad (4)$$

here  $O_{D_x}$ ,  $O_{D_L}$  and  $O_{D_{ML}}$  are the absorbances, at a specific pH value, of the partially formed complex, the free ligand and the fully formed complex, respectively. The absorbance  $O_{D_L}$  of the ligand has been cancelled out, since the same concentration of ligand solution was used as a reference throughout the measurements. The negative logarithm of the concentration of the non-protonated ligand [pL] was obtained using the equation [25]

$$pL = \log_{10} \left( \frac{B_0^H + B_1^H [H^+]}{(T_L - \bar{n}T_m)} \right) \quad (5)$$

where  $B_0^H = 1$ ,  $B_1^H$  is the reciprocal of the acid dissociation constant of the ligand, and  $T_L$  and  $T_m$  are the stoichiometric concentrations of the ligand and the metal ion, respectively. The equation of the formation curve is

$$\bar{n} + (\bar{n} - 1)K_1[L] = 0 \quad (6)$$

TABLE 5

Stability constants for the metal complexes in 50% (v/v) dioxane–water ( $T_m = 5 \times 10^{-5}$  M,  $T_L = 2 \times 10^{-4}$  M,  $pK^H$  ligand = 11.25 at 30 °C)

Complex	$\lambda_{\max}$	pH	$O_{D_x}$	$O_{D_{ML}}$	$\bar{n}$	pL	log $K_1$
Cu(II)– <i>o</i> -OHAHPP	388	3.6	0.32	1.24	0.258	11.378	10.919
		3.8	0.48	1.24	0.387	11.193	10.993
		4.0	0.62	1.24	0.500	11.007	11.007
		4.2	0.76	1.24	0.613	10.821	11.021
		4.4	0.92	1.24	0.742	10.638	11.097
Mean value of log $K_1 = 11.007 \pm 0.05$							
Co(II)– <i>o</i> -OHAHPP	394	4.0	1.00	1.62	0.617	11.022	11.229
		4.5	1.07	1.62	0.660	10.527	10.815
		5.0	1.16	1.62	0.716	10.035	10.436
		5.5	1.24	1.62	0.765	9.541	10.054
		6.0	1.42	1.62	0.877	9.056	9.909
Mean value of log $K_1 = 10.489 \pm 0.48$							

where  $K_1$  is the stability constant of the ML complex. The values obtained for the stability constants ( $\log K_1$ ) using the spectrophotometric method in 50% (v/v) dioxane–water (Table 5) were found to be lower than those obtained in the pH-metric study in 75% (v/v) dioxane–water (Table 3). This decrease in stability values may be due to the different dielectric value of the medium in the two cases.

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