Thermochimica Acta, 113 (1987) 21–29
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMICS AND FORMATION CONSTANTS OF TRIVALENT LANTHANIDE METAL IONS WITH 3-HYDRAZINO-6-PHENYLPYRIDAZINE AND OTHER RELATED DERIVATIVE LIGANDS

BASHEIR A. EL-SHETARY *, MOHAMED S. ABDEL-MOEZ and HESEIN S. SLEEM
Chemistry Deparment, Faculty of Education, Ain Shams University Roxy, Cairo (Egypt)

(Received 1 July 1986)

ABSTRACT

Complexes of trivalent lanthanide metal ions with 3-hydrazino-6-phenylpyridazine (HPP) and its condensation products with benzil (BHPP) and *p*-methoxyacetophonone (*p*-MeOPHPP) have been investigated by pH-metric titration in 75% (v/v) dioxane–water medium at 30°C. The proton ligand stability constant (pK_H) and formation constants ($\log K_1$ and $\log \beta$) were calculated. Moreover, the effects of ionic strength (0, 0.05, 0.1 and 0.15), temperature (20, 30 and 40°C) and the dielectric constant (50, 60 and 75%, v/v, dioxane–water) were evaluated for some selected lanthanide(III)–BHPP complexes. The overall changes in ΔG, ΔH and ΔS were evaluated, and the relation Z^2/r vs. $\log K_1$ of lanthanide complxes was examined.

INTRODUCTION

The azo dyes form the largest group of synthetic dyestuffs and feature in various types of applications. Diketones are well known as good chelating agents, capable of forming stable complexes with metal ions [1,2]. Therefore, the combination of these two classes of complexing agents to form new compounds has the features of both classes of ligands.

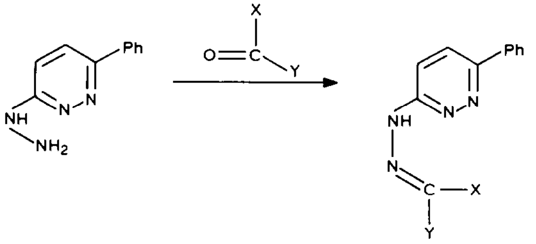
The organic ligands under investigation were prepared by condensing the parent compound 3-hydrazino-6-phenylpyridazine (HPP) through the carbonyl group of both benzil (BHPP) and *p*-methoxyacetophenone (*p*-MeOPHPP). Limited studies have been reported on similar structures, such as isolation of solid complexes [3], characterization of the absorption spectra and stability of chelate compounds of metal ions [4,5]. The present investiga-

---

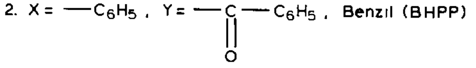
* Author to whom correspondence should be addressed.

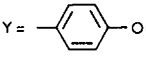
0040-6031/87/$03.50

tion deals with the pH-metric study of chelate formation of trivalent lanthanide metal ions with 3-hydrazino-6-phenylpyridazine (HPP) and its condensed derivatives with diphenylethanedione (benzil) (BHPP) and *p*-methoxyacetophenone (*p*-MeOPHPP) organic ligands. The stability constants have been determined in 75% (v/v) dioxane–water solvent at 30°C and at 0.05 M (KNO_3) ionic strength. The stability constants were determined for selected lanthanide ions at different temperatures to evaluate the thermodynamic constant of the complexes formed. Also, the effect of both solvent and ionic strength were studied.



1 3-Hydrazino-6-phenylpyridazine (HPP)


2. X = $-C_6H_5$, Y = $-\underset{\underset{O}{\|}}{C}-C_6H_5$, Benzil (BHPP)

3 X = $-CH_3$, Y =

OCH_3, *p*-Methoxyacetophenone (*p*-MeOPHPP)

EXPERIMENTAL AND CALCULATIONS

Dissociation constant

pK_H was calculated from:

$$pK_H = B + 0.28 + \log\frac{[HL] + [OH^-]}{[L^-] + [OH^-]} \qquad (1)$$

where B is the pH-meter reading calculated according to Van Uitert et al. [6] and 0.28 the corrected value added in the case of 75% (v/v) dioxane–water solvent as discussed by Irving and Mahnot [7]. Since the ionic product, pK_w, in 75% (v/v) dioxane–water is approximately 18.7 [8], $[OH^-]$ and $[H^+]$ in eqn. (1) are negligible in the region of proton dissociation.

The method adopted by Irving and Rossotti [9] has been employed to determine the parameters $\bar{n}$ and pL. Linear plots of $\log \bar{n}/(1-\bar{n})$ and $\log [2-\bar{n}]/[\bar{n}-1]$ vs. pL were drawn to obtain the best values of $\log K_1$ and $\log K_2$, respectively. The thermodynamic quantities, such as free energy ΔG,

Table 1
Results of elemental analyses of the organic ligands

Compound	Found (calculated)			M.p. (°C)	Colour
	C	H	N		
1-HPP ($C_{10}H_{10}N_4$)	64.90 (64.52)	4.90 (5.38)	30.10 (30.11)	155	Yellow
2-BHPP ($C_{24}H_{18}ON_4$)	76.60 (76.19)	3.80 (4.76)	14.70 (14.81)	170	Yellow
3-*p*-MePHPP ($C_{19}H_{18}ON_4$)	71.90 (71.70)	5.90 (5.66)	18.00 (17.61)	188	Pale yellow

ethalpy ΔH, and entropy ΔS, for the formation constants have been calculated using the relations:

$$\Delta G = -RT \ln K \tag{2}$$

$$\Delta H = \frac{-RT_1T_2}{(T_2 - T_1)} \ln \frac{K_{T_2}}{K_{T_1}} \tag{3}$$

and

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{4}$$

Preparation of the organic ligands

3-Hydrazino-6-phenylpyridazine (HPP) was prepared as mentioned previously [10]. BHPP and *p*-MeOPHPP were obtained by refluxing the 3-hydrazino-6-phenylpyridazine (HPP) with stoichiometric amounts of both benzil and *p*-methoxyacetophenone, respectively, in ethanol for 1 h. The yellow crystals obtained were filtered off, washed with and crystallized from ethanol for HPP and BHPP, and from acetone for *p*-MeOPHPP. The elemental analyses (C, H and N) are shown in Table 1 along with the IR spectra of the organic ligands, confirming the purity of the ligands.

Reagents and materials

Stock solutions of the lanthanide nitrates were prepared and standardized from high-purity BDH lanthanide oxide (99.9%) as mentioned previously [11]. The pH value of metal nitrate solutions was between 4.0 and 4.5. Dioxane (BDH) was freshly distilled over sodium metal and $LiAlH_4$. All chemicals used were of reagent grade. Oxygen-free nitrogen gas was passed through the titrated solutions during all the titrations. The solutions [free ligands and mixtures of ligand and lanthanide(III) ion] were titrated against 0.05 M KOH solution in 75% (v/v) dioxane–water mixtures at constant ionic strength (0.05 M). Furthermore, the following sets of titrations were carried out on Ln(III)–BHPP chelates:

Set I: Ionic strength of 0.15, 0.1 and 0.05 M (KNO_3) in 75% (v/v) dioxane–water mixture at 30 °C.

Set II: Temperatures of 20, 30 and 40°C in 75% (v/v) dioxane–water mixture at ionic strength 0.05 M (KNO_3).

Set III: Solvent ratio 50, 60 and 75% (v/v) dioxane–water at a constant temperature of 30°C and ionic strength 0.05 M (KNO_3).

Corrections for volume changes taking place during the course of titration were made in all cases. The pH-metric titrations were carried out using a WTW digital pH meter fitted with a combination electrode. The pH meter was calibrated using standard BDH buffered solutions. Values of the thermodynamic dissociation constants, log K_H^0, were obtained by extrapolating the curve of log K_H vs. $\sqrt{\mu}$ to zero. This value of log K_H^0 was used to calculate the stability constants for Ln–BHPP complexes at zero ionic strength.

RESULTS AND DISCUSSION

(i) Formation constants of Ln(III) chelate compounds

The proton ligand dissociation constants are summarized in Table 2. The mole ratio of metal ion ligand (HL) was kept constant at 1 : 2. In the initial

TABLE 2

Formation constants of 1 : 1 and 1 : 2 tetravalent lanthanide metal ion–X (3-hydrazino-6-phenylpyridazine ligand) complexes in 75% (v/v) dioxane–water mixtures at 30 ± 0.05 °C and $\mu = 0.05$ M KNO_3

Ln(III) cation	X = benzil (BHPP)		X = *p*-methoxy-acetophenone (*p*-MeOPHPP)		X = H_2 (parent) HPP		X = benzil [a] (BHPP)	
	log K_1	log β	log K_1	log β	log K_1	log β	log K_1	log β
pK_H	12.62	–	13.25	–	13.08	–	12.69	–
La	8.05	16.28	8.55	17.20	8.80	17.68	8.18	16.43
Pr	8.50	17.13	9.12	18.34	9.48	18.79	8.56	17.25
Nd	8.42	17.02	9.02	18.21	9.36	18.67	8.90	17.91
Sm	8.85	17.95	9.27	18.82	9.65	19.36	9.02	18.24
Eu	8.77	17.79	9.41	19.06	9.73	19.51	9.11	18.32
Gd	8.83	17.97	9.36	18.96	9.67	19.33	9.03	18.27
Tb	9.06	18.40	9.61	19.44	9.75	19.59	9.30	18.83
Dy	9.08	18.42	9.62	19.51	9.79	19.60	9.36	18.95
Ho	9.15	18.54	9.78	19.90	9.76	19.59	9.35	18.99
Er	9.18	18.65	9.93	20.16	9.79	19.69	9.48	19.12
Yb	9.36	19.02	10.04	20.40	9.94	20.04	9.71	19.70

[a] The measurements were carried out at zero ionic strength.

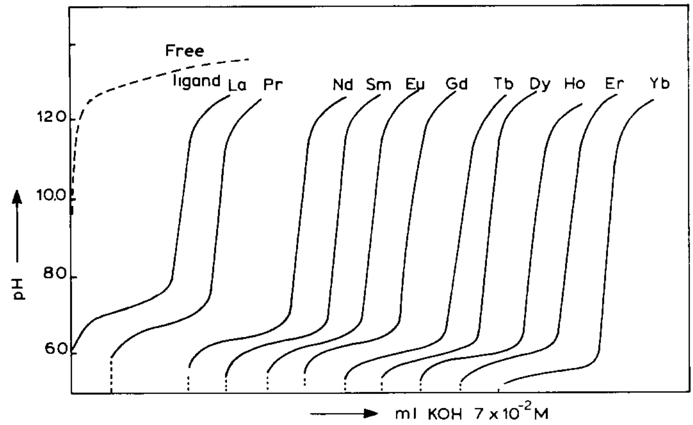


Fig. 1. pH-metric titration curves of BHPP (3×10^{-3} M) in the absence and presence of Ln(III) ions (1.5×10^{-3} M) at 30°C in 75% (v/v) dioxane–water mixtures. Initial values, $V^0 = 30$ ml.

stage of titration the metal–ligand titration curves are depressed by about 4 pH units compared to that of the ligand titration curves due to complex formation and liberation of protons. The titration curves for the ligand–metal mixture show only one sharp inflection and $m = 2$ (m = number of moles of KOH added per mole of ligand), Fig. 1. This confirms that all ligands behave as monoprotic ligands 1, 2 and 3 as shown from the schematic equilibrium. The titration of 1 : 3 and 1 : 5 metal/ligand ratio of some lanthanide ions always gives an inflection at $m = 2$. This supports the idea that complexes of 1 : 2 metal/ligand ratio are predominant.

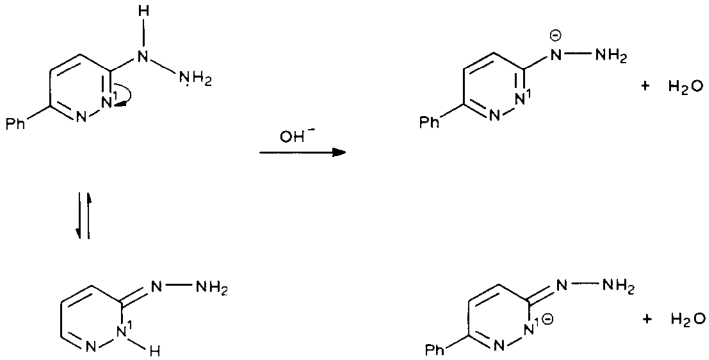


Figure 2 gives a plot of the formation constant (log K_1) for the lanthanide complexes against ionic potential Z^2/r. Instead of the expected linearity, attributed to the formation electrostatic interaction, a curve is obtained with gradual increase in stability between La and Eu followed by a small decrease in the Tb–Tm region. This kind of behaviour has been observed before for a

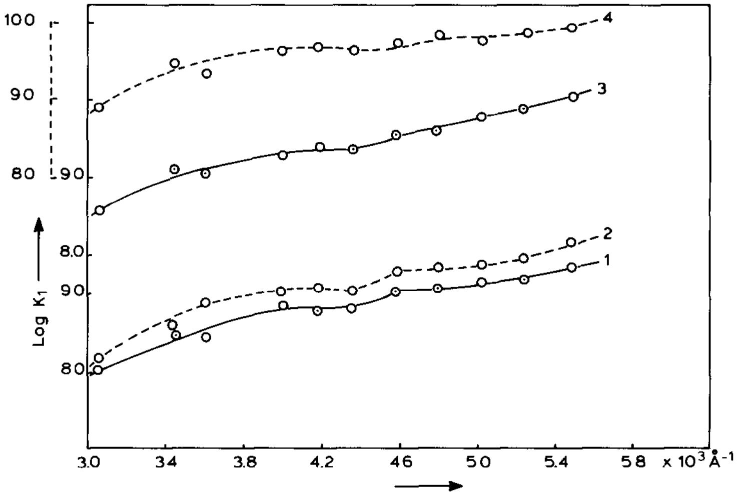


Fig. 2. Log K_1 as a function of ionic potential Z^2/r for lanthanide(III) complexes at 30 °C, $\mu = 0.05$ M in 75% (v/v) dioxane–water mixtures. 1, Ln(III)–BHPP; 2, Ln(III)–BHPP (zero ionic strength); 3, Ln(III)–*p*-MeOPHPP; 4, Ln(III)–HPP.

variety of chelating agents [4,5,12,13]. This deviation from linearity beyond gadolinium has been attributed by various authors to changes in hydration along the cationic series [14–16]. The similarity in behaviour of the ligands studied with that cited in the literature [4,5,12,13] is due to the presence of similar sites in the ligands. BHPP is expected to form chelates with lanthanide ions by using the carbonyl oxygen atom of benzil, the nitrogen atom of the azomethine group and the nitrogen atom (N^1) of the pyridazine ring.

The overall formation constants of Ln(III) chelates (Table 2) follow the order: HPP > *p*-MeOPHPP > BHPP, which is proportional to the values of log K_H. The observed order is in agreement with the electron-withdrawing property of the carbonyl group and the electron-releasing effect of the methoxy group. The slight increase in stability values of the HPP chelates relative to *p*-MeOPHPP chelates may be attributed to the difference in size of the chelating rings (Table 2).

Effect of ionic strength

To investigate the nature of interactions between the metal ion and the ligands, the metal–ligand stability constants were determined at 0.00, 0.05, 0.10 and 0.15 M ionic strength at 30 °C. This study of the dependence of formation constants on ionic strength showed that there is a regular and slow decrease in the values of the formation constants with increasing ionic strength, which is in agreement with the trend in the variation of pK_H of the BHPP ligand (Table 3A). It is seen that at different ionic strengths the

TABLE 3

Stepwise formation constants for the formation of 1:1 and 1:2 lanthanide(III)–BHPP chelates under different conditions

(A) At 30°C in 75% (v/v) dioxane–water and different ionic strengths

Ln(III) cation	μ = zero		μ = 0.05 M		μ = 0.10 M		μ = 0.15 M	
	$\log K_1$	$\log \beta$	$\log K_1$	$\log \beta$	$\log K_1$	$\log \beta$	$\log K_1$	$\log \beta$
pK_H	12.69	–	12.62	–	12.52	–	12.46	–
Nd	8.90	17.91	8.42	17.02	8.39	16.99	8.23	16.69
Eu	9.11	18.32	8.77	17.79	8.55	17.27	8.40	16.98
Er	9.48	19.17	9.18	18.65	9.08	18.45	8.91	18.10
Yb	9.71	19.70	9.36	19.02	9.21	18.74	9.10	18.52

(B) At μ = 0.05 M in 75% (v/v) dioxane–water and different temperatures

Ln(III) cation	Temp. (°C)	pK_H	Formation constants		$-\Delta G$ (kcal mol^{-1})	$-\Delta H$ (kcal mol^{-1})	ΔS (J mol^{-1})
			$\log K_1$	$\log \beta$			
Nd	20	12.98	8.76	17.72	23.76	29.94	0.177
	30	12.62	8.42	17.02			
	40	11.94	8.07	16.39			
Gd	20	12.98	9.10	18.46	24.92	27.64	0.173
	30	12.62	8.83	17.97			
	40	11.94	8.48	17.18			
Ho	20	12.98	9.37	19.02	25.77	27.64	0.177
	30	12.62	9.15	18.56			
	40	11.94	8.81	17.87			

(C) At 30°C and μ = 0.05 M and different dioxane–water ratios

Ln(III) cation	50% (v/v)		60% (v/v)		75% (v/v)	
	$\log K_1$	$\log \beta$	$\log K_1$	$\log \beta$	$\log K_1$	$\log \beta$
pK_H	11.24	–	11.68	–	12.62	–
Nd	6.84	13.80	7.38	14.93	8.42	17.02
Eu	7.30	14.70	7.83	15.87	8.77	17.79
Er	7.68	15.47	8.21	16.56	9.18	18.65
Tb	7.90	15.94	8.47	17.15	9.36	19.02

overall formation constants of Ln(III) chelates follow the order: Nd(III) < Ed(III) < Er(III) < Yb(III).

Effect of temperature

The values of ΔH, ΔG and ΔS have been calculated from the formation constants of Ln(III)–BHPP complexes obtained at different temperatures

(20, 30 and 40 °C) using the Gibbs–Helmholtz equation (Table 3B). The ΔH values were obtained from plots of log K_1 vs. $1/T$. The negative values of ΔH show that the reactions of these metals with BHPP ligand are exothermic. Since the complex formation reaction is unfavourable at higher temperatures, the values of both log K_1 and log β (overall formation constant) decrease with temperature increase. The ΔG values are negative for all the chelates showing that these reactions are spontaneous. The ΔS values are positive for all of the chelates showing that the entropy is favourable for complex formation [17].

Effect of dielectric constants on stability

Other important factors influencing the stability constants of the metal chelates are the dielectric constant of the medium and the solvating property of the solvent. An attempt has been made to investigate the effect of variation of the dielectric constant on the stabilities of complexes of lanthanide metal ions with BHPP ligand in various dioxane–water mixtures (50, 60 and 75%, v/v). The formation constants of the selected lanthanide chelates in different dioxane–water mixtures are recorded in Table 3C. It is seen that with increasing, organic content of the solvent the stability constants increase. This is similar [18] to the ligand containing oxygen–metal links: the stabilities increased with increasing organic content of the solvent. However, the reported effect [19] of the solvent on complexes containing nitrogen–metal links concluded that the organic content of the solvent had little influence on the stabilities of the complexes. The formed complexes containing both oxygen–metal and nitrogen–metal links and the observed increase in the stabilities may be due to the oxygen–metal link, which is strongly affected [14,17,20].

REFERENCES

1 A.E. Martill and R.M. Smith, Critical Stability Constants, Vol. 3, Plenum Press, New York, 1977.
2 D.D. Perrin, Stability Constants of Metal-Ion Complexes, Part B, Organic Ligands, IUPAC Chemical Data Series, No. 22, Pergamon Press, Oxford, 1979.
3 A.K. Jain, R.N. Gayal and D.D. Agawal, J. Inorg. Nucl. Chem., 43 (1981) 2005.
4 A.T. Ramadan, M.H. Seada and E.N. Rizkalla, Talanta, 30 (1983) 245.
5 E.N. Rizkalla, A.T. Ramadan and M.H. Seada, Polyhedron, 2 (1983) 1155.
6 L.G.C. Van Uitert, G.G. Hass, W.C. Fernelius and B.E. Douglas, J. Am. Chem. Soc., 75 (1953) 457.
7 H.M.N.H. Irving and U.S. Mahnot, J. Inorg. Nucl. Chem., 30 (1968) 1215.
8 D.E. Goldberg, J. Chem. Educ., 40 (1963) 341.
9 H. Irving and H.S. Rossotti, J. Chem. Soc., (1953) 3397; (1954) 2904.
10 H. Jahine, H.A. Zaher, A. Sayed and M.H. Seada, Indian J. Chem., 15B (1977) 352.
11 A.M. Zahra, B.A. El-Shetary and A. Ismail, J. Chin. Chem. Soc., 27 (1980) 37.

12 F.H. Spedding, J.E. Powell and J.W. Wright, J. Am. Chem. Soc., 78 (1956) 34.
13 T.F. Gritmon, H.P. Goedken and G.R. Choppin, J. Inorg. Nucl. Chem., 39 (1977) 2021.
14 G. Degischer and G.R. Choppin, J. Inorg. Nucl. Chem., 34 (1972) 2823.
15 I. Grenthe, Acta Chem. Scand., 18 (1964) 293.
16 L.A.K. Staveley, D.R. Marhan and M.R. Jones, J. Inorg. Nucl. Chem., 30 (1968) 231.
17 R.N. Kasi Viswanathan and M.G. Reddy, J. Indian Chem. Soc., 61 (1984) 856.
18 L.G. Van Uitert, W.C. Fernelius and B.E. Douglas, J. Am. Chem. Soc., 75 (1953) 2739.
19 F. Basolo and R.K. Murmann, J. Am. Chem. Soc., 74 (1952) 5243.
20 H. Irving and H.S. Rossotti, Acta Chem. Scand., 10 (1956) 72.