

CHELATING ABILITY OF SOME SUBSTITUTED 4-PYRAZOLONE DYES TOWARDS TRIVALENT LANTHANIDE IONS

Part I. Structure-Stability Relationships

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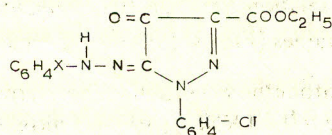
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Acid dissociation constants, pK_i of a series of substituted 4-pyrazolone dyes (Ia - e) have been determined potentiometrically in 70% (v/v) dioxane - water at 30° and 0.1M ionic strength. The stability constant of their 1:1 and 1:2 chelates with five-trivalent lanthanide ions Ln(III) have also been determined. The effect of substituents on the hydrazo-moiety of the ligand on the equilibria are discussed. The data were correlated and the results were taken to explain the stabilization of such chelates by dative π -bonding between Ln(III) and the ligand.

INTRODUCTION

Question about the involvement of metal ligand complexes in medical treatment are of special interest [1], especially structure stability relationship. Pyrazolones were used as analgetics and antipyretics, where the most commercial use of it is as dyes. Snavelly *et al.* [2] determined potentiometrically the relative stabilities of the metal derivatives of simple aryl-azo-5-pyrazolones. Structure stability relationship of some substituted 4-pyrazolone dyes chelates with Cu(II) and Ni(II) has recently been reported [3]. In continuation of our studies, we have investigated the effects of substituents on the chelating tendency of a series of 4-pyrazolone dyes (Ia-e) towards some lanthanide ions Ln(III). In addition the applicability of Hammett equation to correlate the stability constants of Ln(III)-4-pyrazolone dyes complexes should be discussed.

The hydrazo-structure of the ligands (Ia-e) has been confirmed [4].



4-Pyrazolone -1-(4-chlorophenyl)-3-carboethoxy-5-hydrazonyl (Ia-e, HL) [(a) X = 4-OCH₃ (m.p. 90°); (b) X = 4-CH₃ (m.p. 136°); (c) X = 4-NO₂ (m.p. 248°); (d) X = 3-NO₂ (m.p. 159°); (e) X = 3-Cl (m.p. 129°)].

EXPERIMENTAL

Substituted 4-pyrazolone dyes (Ia-e) were prepared as described earlier (3). Each of the ligands was tested for

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purity. A set of 0.1M solutions of the ligands were prepared in dioxane previously purified [5]. Dioxane-water mixture (70% v/v) was used to prepare KOH (0.02M) carbonate free. Solution of Ln(NO₃)₃ were obtained and complexometrically determined by the method previously described [6]. Potassium nitrate of A.R. grade (B.D.H.) was used to adjust the ionic strength at 0.1M.

Titrations were performed using a radiometer pH-meter type 63 fitted with a combined glass electrode (type GK 2301 C). The instrument was precise to ± 0.01 pH unit. It was calibrated using two standard Beckman buffer solutions at pH 4.01 and 7.00. Titration was carried out at 30° and 0.1M ionic strength using the technique used by us [7]. The pH-meter readings (B) recorded in 70% (v/v) dioxane-water solutions were converted to hydrogen ion concentration [H⁺] by means of the widely used relation of van-Uitert and Haas [8], namely

$$-\log [H^+] = B + \log U_H \quad (1)$$

where U_H is the correction factor for the solvent composition and ionic strength for which B is read, and was found to be +0.15 at 30° and 0.1M ionic strength.

RESULTS

The stoichiometric acid dissociation constant pK_i ; of each ligand can be calculated from the pH data by equation:

$$K_i = \frac{[H^+] (aT_L + [H^+] - [OH^-])}{T_L (1-a) - [H^+] + [OH^-]} \quad (2)$$

where T_L is the analytical concentrations of the ligand and a is the ratio of the mole of base added to mole of ligand.

The values of $[H^+]$ and $[OH^-]$ are very small compared with the values of $[KOH]$ and T_L . It follows that

$$K_i = \frac{[H^+] a}{(1-a)} \quad (3)$$

The results of computation are given in Table 1. The average values of pK_i computed by this way were reproducible to between ($\pm 0.01-0.03 pK_i$). The stoichiometric stability constants ($\log \beta_n$) of Ln(III) chelates were computed from the titration data using the method of Rossotti and Rossotti [9].

$$\frac{\bar{n}}{(1-\bar{n}) [L^-]} = \beta_1 + \beta_2 \frac{(2-\bar{n}) [L^-]}{(1-\bar{n})} \quad (4)$$

where,

$$[L^-] = \frac{(1-a) T_L - [H^+] + [OH^-]}{[H^+]/K_i}$$

and

$$n = \frac{T_L - [L^-] ([H^+]/K_i + 1)}{T_M}$$

In this equations, T_L and T_M refer to the total ligand and metal concentration used respectively; \bar{n} , the average number of ligand atoms bound to the metal ion. Fig. 1 illustrates the titration experimental curves as a typical example.

Formation of polynuclear complexes is excluded because the experimental points of each series defined only one curve $\bar{n}/[L^-]$ vs. $[L^-]$ as shown in Fig. 2 for Sm(III)-Ib chelates. The values of \bar{n} and $[L^-]$ were calculated up to precipitation. The values of \bar{n} does not exceed 2 under our experimental condition. Consequently a plot of $\bar{n}/(1-\bar{n})$ vs. $(2-\bar{n}) [L^-]/(1-\bar{n})$ is a straight-line of intercept β_1 and slope β_2 . Using the least square method [10] the computed values are listed in Table 1. The uncertainties in the values

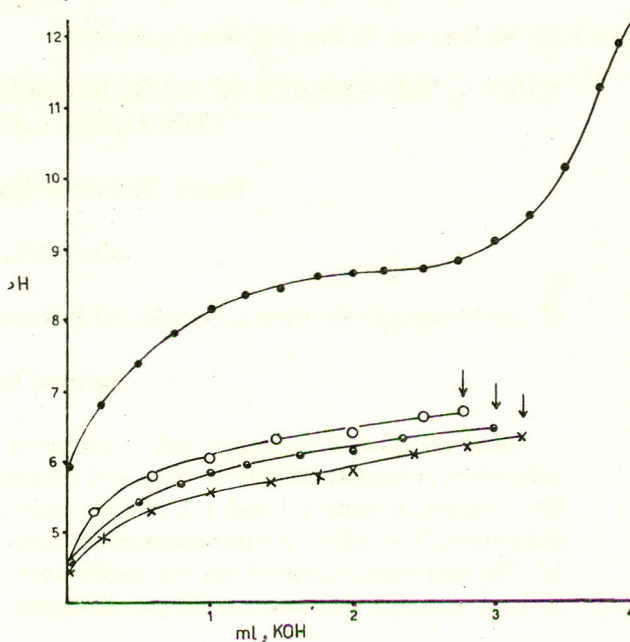


Fig. 1. Titration curve of I_a chelates with Sm(III) in 70% (v/v) dioxane-water mixture at 30°C, $\mu = 0.10$ KNO₃; ● ligand alone $3.0 \times 10^{-3} M$, $[Sm^{+3}] = 1.0 \times 10^{-3} M$, [HL], ○: $2 \times 10^{-3} M$, ◐: $3 \times 10^{-3} M$, X: $5 \times 10^{-3} M$.

of β_1 and β_2 due to possible hydrolysis of the central ion appear to be negligible over the experimental range. The presence of only 1:1 and 1:2 chelates over the experimental range proved correct as invariant values of β_1 and β_2 were obtained at different concentrations of the reactants. The linearity observed between $\log \beta_1$ and $\log \beta_2$ values and pK_i or substituent σ constant confirmed *a posteriori* the correctness of this assumption.

DISCUSSION

Calculated pK_i values (Table 1) show that it depends on the nature of the substituent on the phenylhydrazo-moiety. The relation between the Hammett substituent σ and the pK_i values (Fig. 3) follows the equation:

Table 1. Acid dissociation constants of 4-pyrazolone-1-(4-chlorophenyl)-3-carboethoxy-5-hydrazonyl derivatives (I_a-e) and stability constants ($\log \beta_n$) of their lanthanide chelates ($30 \pm 0.1^\circ$, $\mu = 0.10$ KNO₃, 70% v/v dioxane-water)

Ligand	σ	pK_i^*	$\log \beta_1^\dagger$					$\log \beta_2^\dagger$				
			Pr	Nd	Sm	Gd	Er	Pr	Nd	Sm	Gd	Er
I _a	-0.268	9.25		5.85					11.70			11.51
I _b	-0.17	8.84	5.78	5.85	5.23	5.48	5.51	11.46	11.65	10.53	10.98	11.01
I _c	+0.37	8.03	5.27	5.25	4.99	4.59	4.99	10.69	11.00	10.43	10.15	10.15
I _d	+0.71	7.54		4.73					10.74			9.90
I _e	+0.778	7.34		5.14			4.81		10.38			9.03

* Standard deviation in $pK_i \pm 0.03$; † Standard deviation in $\log \beta_n \pm 0.05-0.09$.

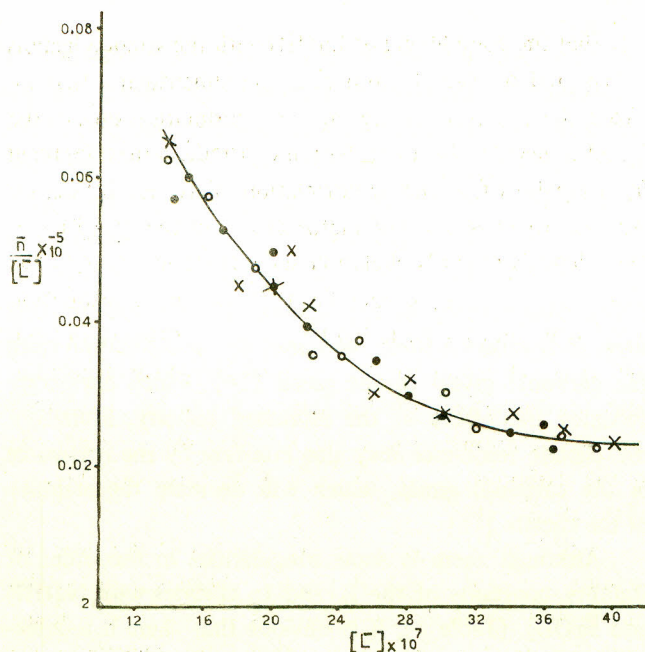


Fig. 2. $\bar{n}/[L^-]$ vs. $[L^-]$ for Sm(III) - I_p systems in 70% (y/v) dioxane-water mixture at 30° , $\mu = 0.10$ KNO_3 , $[\text{Sm}^{+3}] = 1 \times 10^{-3} M$, $[\text{HL}]$, X: $2 \times 10^{-3} M$, O: $3 \times 10^{-3} M$, \bullet : $5 \times 10^{-3} M$.

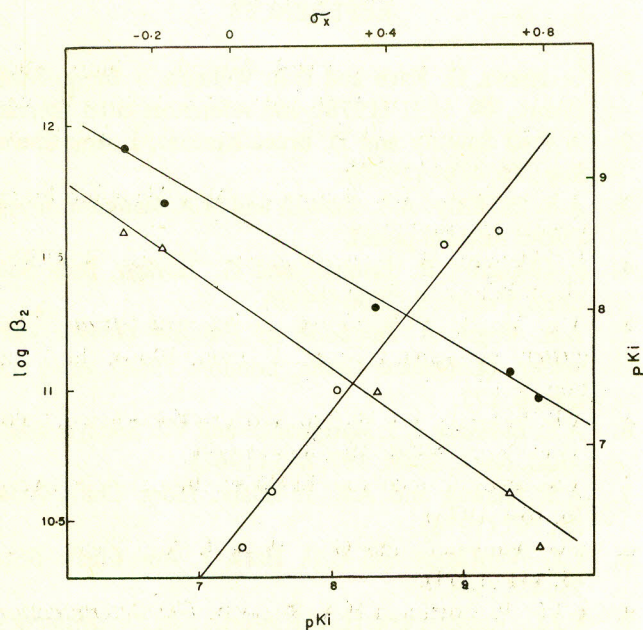


Fig. 3. Correlation of $\log \beta_2$ for Nd(III) chelates with pK_i and the Hammett substituent σ_x , \bullet : pK_i vs. σ_x , O: $\log \beta_2$ vs. pK_i , Δ : $\log \beta_2$ vs. σ_x .

$$pK_i = 8.68 (\pm 0.02) - 1.68 (\pm 0.05) \sigma_x \quad (5)$$

with the correlation coefficient $r = 0.99$. Comparison of the values of the reaction constants, defined by the slopes of the linear correlations for the bases $\text{Ar} - \bar{N} - \text{N} = \text{C} - (\text{L}^-)$ and ArCOO^- (1.68 and 1.74 [11] respectively) indicates that the $\text{Ar} - \text{N}$ link appears transmitting substituent effects with 91% efficiency measured by the ratio $\rho_{\text{Ar} - \bar{N} - \text{N} = \text{C} - / \rho_{\text{ArCOO}^-}$. The negative value for ρ , indicates that the dissociation constant of the studied ligands

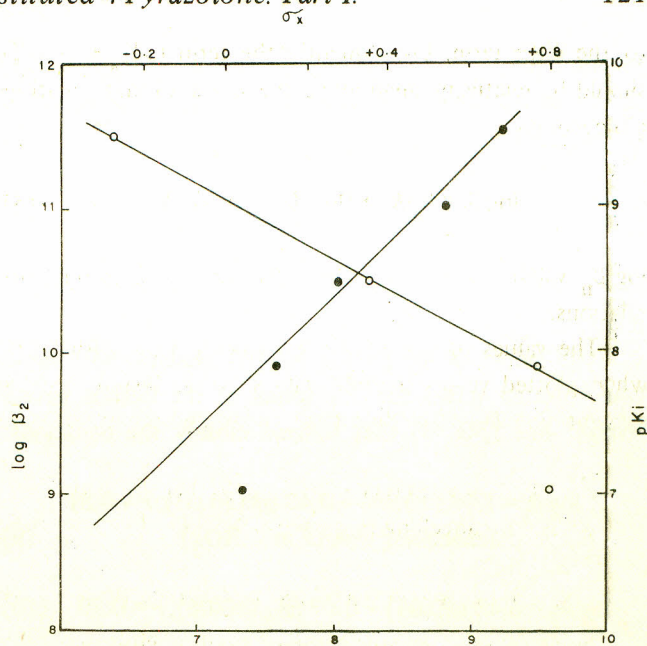


Fig. 4. Relationships between $\log \beta_2$ for Er(III) chelates with pK_i and σ_x , O: $\log \beta_2$ vs. pK_i , \bullet : $\log \beta_2$ vs. σ_x .

are not facilitated by electron-withdrawing substituents, while value of ρ , more than unity is obtained since the polar effect of the substituents are operating on the nitrogen atom directly adjacent to the benzene ring.

As the relation between the metal ion and the ligand is regarded as a Lewis acid-base reaction, the correlation between the values of pK_i for the ligands Ia-e and the stoichiometric stability constants of their chelates with Nd(III) and Er(III) as a typical examples were examined. The use of conditional equilibrium constants ($\log \beta_n$ and pK_i) rather than the thermodynamic equilibrium constants ($\log {}^T\beta_n$ and $p{}^T K_i$) can be justified as follows. The relation between the $p{}^T K_i$ of a series of ligands and $\log {}^T\beta_1$ of their 1:1 metal chelates has been shown [12] to be

$$\log {}^T\beta_1 = b p{}^T K_i + \log {}^T\beta_{10} - b p{}^T K_{i0} \quad (6)$$

where o refers to the unsubstituted ligand. In terms of the conditional equilibrium constants, the latter relation becomes:

$$\log \beta_1 = b pK_i + (\log \beta_{10} - b pK_{i0} + (b Y_{H^+} - Y_M)) \quad (7)$$

where $Y_{H^+} = \log (f_L/f_{L0}) + \log (f_{ML}/f_{HL})$

and $Y_M = \log f_{L0}/f_L + \log f_{ML}/f_{ML0L0}$

In the above equations, b , is a constant and f_i term refers to the activity coefficient of the species i . It may be assumed [12] under the same condition, that $f_{L0} \cong f_{ML0}$, so that the Y_M is close to zero. The same argument applies

to the Y_{H^+} term. Consequently the term $(bY_{H^+} - Y_M)$ should be relatively small along the series, so that equation (7) becomes

$$\log \beta_1 = bpK_i + (\log \beta_{10} - b pK_{ii}) \quad (8)$$

$\log \beta_n$ values calculated graphically were used in our correlations.

The values of $\log \beta$ for Nd(III) chelates with Ia–e, when plotted versus the pK_i values of the ligands, gave a straight line (Fig. 3) that follows closely the equations:

$$\log \beta_1 = 1.93 (\pm 0.04) + 0.43 pK_i (0.03), r = 0.81$$

(cancelling that of $m - NO_2$) (9)

$$\log \beta_2 = 5.48 (\pm 0.04) + 0.67 pK_i (\pm 0.06), r = 0.80 \quad (10)$$

Similarly $\log \beta_n$ for Er(III) chelates with the same series of ligands were linearly correlated with pK_i values of such ligands. The relation can be expressed by equations (11,12), (cancelling that of $p - NO_2$) (Fig. 4).

$$\log \beta_1 = -1.33 \pm (0.07) + 0.78 pK_i \pm (0.04), r = 0.90 \quad (11)$$

$$\log \beta_2 = 3.28 (\pm 0.041) + 0.89 pK_i (\pm 0.07), r = 0.91 \quad (12)$$

The observed linear relationship imply that the stability constant of lanthanide chelates is governed by the acidity of the ligands used. The slope values of the above relation, $\log \beta_n$, versus pK_i , calculated by the least square method were less than unity, suggesting that, Ln(III) ions acts as π -electron donor [13]. Consequently the formed complexes are stabilized by back donation from the metals to the ligands.

Next the applicability of Hammett equation to $\log \beta_1$ and $\log \beta_2$ values of chelates of Nd(III) and Er(III) as a typical example was examined. In both cases plot of $\log \beta_1$ or $\log \beta_2$ (which are illustrated in Figs. 3,4) versus the substituent constant, σ_x . The equations of the regression lines obtained are:

$$\log \beta_1 (\text{Nd}) = 5.66 (\pm 0.07) - 0.76 (\pm 0.08),$$

$$r = 0.76 \text{ (omitting that of } m\text{-NO}_2\text{)} \quad (13)$$

$$\log \beta_2 (\text{Nd}) = 11.43 (\pm 0.04) - 1.17 (\pm 0.05),$$

$$r = 0.79 \quad (14)$$

$$\log \beta_1 (\text{Er}) = 3.95 (\pm 0.06) - 1.09 (\pm 0.08),$$

$$r = 0.78 \quad (15)$$

$$\log \beta_2 (\text{Er}) = 10.97 (\pm 0.06) - 1.46 (\pm 0.08)$$

$$r = 0.89 \text{ (omitting that of } p - NO_2\text{)} \quad (16)$$

Negative slopes of the previous regression lines, indi-

cate that the complexing of Ln(III) with the studied ligands is favoured by the electron releasing substituents that increase the electron density on the coordination sites of the ligand molecule. Such correlation contradicts that obtained from previous free energy correlation. This may be suggested that there is another factor affecting the affinities of these ligands towards chelation such as steric effect of the bulky groups being in the ligands near the coordination sites, as it causes a steric hindrance to coordination from the carbonyl group to the metal [14], which over compensates the effect of the increased basicity. Moreover, the chelate resonance may also interfere by the resonance in the carbonyl group, which will decrease the stability of the chelate [15].

Although there is some irregularities in the order of stability constants of the I_b and I_c chelates with Nd(III) and Er(III), (Table 1), it is obvious that there is a detectable difference in the values of $\log \beta_n$ for two successive metals.

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