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Copper(II) and Nickel(II) Chelates with some Substituted 4-Pyrazolone Dyes in Dioxane–Water Medium. Structure Stability Relationships

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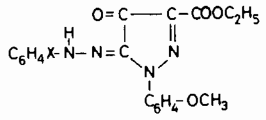
Acid dissociation constants, pK_i of a series of 4-pyrazolones (Ia–f) has been determined potentiometrically in 70% (v/v) dioxane-water media at 30 °C and 0.1 M *ionic strength. The stability constants, $\log\beta_1$ and $\log\beta_2$ of their copper(II) and Ni(II) chelates have also been determined. The effects of substituents on the ligand dissociation were discussed. Both values of pK_i and $\log\beta_n$ were linearly correlated with Hammett substituent, σ. The equations of the straight lines obtained are: $pK_i = 8.758 - 1.911\sigma$ ($r = 1$); $\log\beta_1$ Cu(II) $= 8.25 - 0.99\sigma$ ($r = 0.980$); $\log\beta_2$ Cu(II) $= 15.131 - 1.82\sigma$ ($r = 0.999$); $\log\beta_1$ Ni(II) $= 5.931 - 1.07\sigma$ ($r = 0.899$); $\log\beta_2$ Ni(II) $= 12.53 - 1.28\sigma$ ($r = 0.911$).*

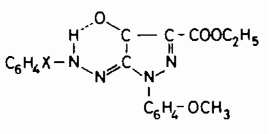
Introduction

In spite of the enormous number of stability constant data available in the literature, nothing has appeared in the literature concerning the relationship between the structure of 4-pyrazolone-1-aryl-3-carbethoxy-5-hydrazonyl derivatives (Ia–f) and the stability of their metal chelates. This paper reports the results of a potentiometric study of the acid dissociation constants of a series of six of the above mentioned ligands (1a to 1f) and the stability constants of 1:1 and 1:2 complexes (metal:ligand) formed between each of these ligands with copper(II) and nickel(II) in correlation with their structure.

Recently during the study of the structure of aryl azopyrazolones [1] it was found that these compounds are capable of keto–enol tautomerism which results in the formation of six membered chelate ring and the hydrazo-structure predominates, so our ligands can be found in the forms I and II:



I (HL)



II

a, X = 4 - OCH_3
b, X = 4 -CH_3
c, X = H
d, X = 4 - NO_2
e, X = 3 - NO_2
f, X = 3 - Cl

The present investigation was undertaken to obtain quantitative information pertinent to the electronic effect on the stability of Cu(II) and Ni(II) chelates caused by substituents in *meta* and *para* positions of the hydrazo moiety of I. Due to the limited solubility of these ligands and their metal chelates in aqueous medium, measurements were carried out in 70% (v/v) dioxane–water solutions.

Experimental

Materials

The azo compounds were prepared by coupling the appropriate diazotized amines to 1-phenyl-3-carbethoxy-4-pyrazolone as previously described [1]. The melting points for ligands are 141, 127, 212, 171, 166 °C, respectively. Each of the ligands was tested for purity. A set of 0.10 *M* solutions of the ligands were prepared in previously purified dioxane [2]. Dioxane–water (70% v/v) mixture was used in preparing potassium hydroxide (0.02 *M*). Stock solution of $Cu(NO_3)_2$ and $Ni(NO_3)_2$ were checked complexometrically [3]. Potassium nitrate of *A.R.* grade of B.D.H. was used to adjust the ionic strength at 0.1 *M*.

Measurements and Procedure

A radiometer pH-meter 63 (accurate to ±0.001pH units) equipped with a combined glass electrode type (GK 2301 C) was used to record the hydrogen ion concentration.

The titration technique was as follows: 50 ml of a solution with a metal ion concentration of 2.0 to 10 × 10^{-3} *M* and KNO_3 in an amount to give ionic

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strength equal to 0.1 *M* were transferred to a 100 ml capacity water-jacketed cell which was thermostated at 30 ± 0.1 °C. Potassium hydroxide (0.02 *M*) was added in small increments through a Jurgens micro burette precise to ±0.05 ml. Purified nitrogen was bubbled in the solution before and during the titration. The pH of the solution was read after each addition of base and the lapse of sufficient time for attainment of equilibrium. The titration was continued to pH ≈ 12 or until visual precipitation occurred. All titrations were repeated at least twice and agreement between pH readings of different titrations was usually within ±0.01. The pH meter readings (B) in dioxane–water (70% v/v) medium were converted into hydrogen ion concentration by means of equation (1):

$$-\log[H^+] = B + \log U \qquad (1)$$

where logU is the correction factor at a given temperature [4]. The value of logU in 70% (v/v) dioxane–water at 30 °C and 0.1 *M* ionic strength was determined to be ±0.15.

Results and Discussion

The potentiometric titration curves of ligands with Cu(II) and Ni(II) show that there is an inflection at a, the number of mol of base added per mol of the ligand, equal to one and accordingly the dissociation of the acid–base equilibrium of these 4-pyrazolone derivatives (HL) may be represented as follows:

$$HL \rightleftharpoons H^+ + L^-$$

$$K_i = \frac{(H^+)(L^-)}{(HL)} \qquad (2)$$

The pK_i value of the ligand HL was calculated using the equation:

$$K_i = \frac{(aT_L + [H^+] - [OH^-])[H^+]}{T_L[1 - a] - [H^+] + [OH^-]} \qquad (3)$$

where T_L is the analytical concentration of the ligand. The results of computation are given in Table I.

In all the calculations the concentrations were corrected for change of volume produced by the addition of potassium hydroxide solution. The average values of the pK_i computed by this way were reproducible to ±0.01–0.03 pK unit.

The reaction equilibria and their equilibrium constants which fit the observed experimental data may be represented as follows:

$$L^- + M^{2+} \rightleftharpoons ML^+;\ K_1 = \frac{[ML^+]}{[ML^+][L^-]} \qquad (4)$$

$$ML^+ + L^- \rightleftharpoons ML_2;\ K_2 = \frac{[ML_2]}{[ML^+][L^-]} \qquad (5)$$

where $K_1 = \beta_1$ and $K_iK_2 = \beta_2$

The 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. 1 for Cu(II)–1a chelates. The method of Rossotti and Rossotti [6] was also used for evaluating the values of the stability constants β_1 and β_2 using the equation:

$$\frac{\bar{n}}{(1 - n)(L^-)} = \beta_1 + \beta_2 \frac{(2 - \bar{n})[L^-]}{(1 - n)} \qquad (6)$$

where

$$[L^-] = \frac{(1 - a)T_L - [H^+] + [OH^-]}{(H^+)/K_i} \qquad (7)$$

and

$$\bar{n} = \frac{T_L - [L^-]([H^+]/K_i + 1)}{T_M} \qquad (8)$$

In these equations, T_L and T_M refer to the total ligand and metal ion concentrations used respectively, and $\bar{n}$ to the average number of the ligand atoms bound to the metal ion.

TABLE I. Acid Dissociation Constant (pK_i) of 4-Pyrazolone-1-aryl-3-carbethoxy-5-hydrazonyl and the Stability $\log\beta_n$ (Calculated Graphically) of Their Cu(II) and Ni(II) Chelates in 70% Dioxane–Water Medium at 30 °C, μ = 0.1 *M*.[a]

Ligand	pK_i	σ	Cu(II)		Ni(II)	
			$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$
p-OCH$_3$	9.30	−0.268	8.418	15.632	6.229	12.821
p-CH$_3$	9.04	−0.17	8.549	15.449	6.269	12.833
H	8.75	0	8.281	15.162	5.801	12.212
m-Cl	8.07	+0.37	7.794	14.393	6.985	13.999
m-NO$_2$	7.42	+0.71	7.613	–	4.225	12.003
p-NO$_2$	7.25	+0.778	7.494	13.753	5.945	11.562

[a] Standard deviation, s, in pK_i ± 0.01–0.03; $\log\beta_1$ ± 0.1–0.15; $\log\beta_2$ ± 0.1–0.2.

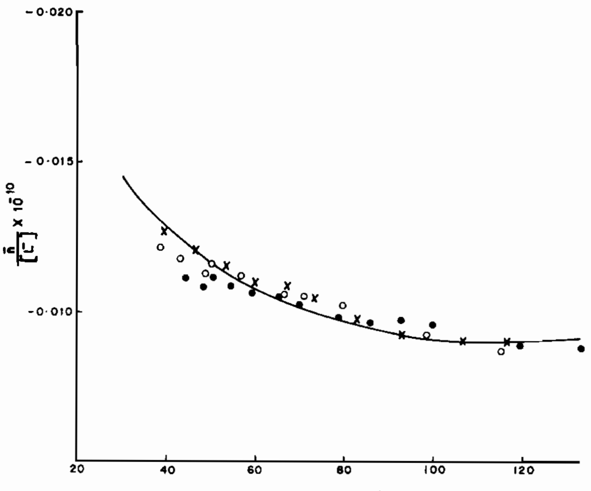

Fig. 1. Curves $\bar{n}/[L]$ *vs.* $[L]$ for Cu(II) and 1a system (μ = 0.1 *M*). X: $[HL] = 2 \times 10^{-3}$ *M*, $[Cu^{2+}] = 1 \times 10^{-3}$ *M*. ○: $[HL] = 3 \times 10^{-3}$ *M*, $[Cu^{2+}] = 1 \times 10^{-3}$ *M*. ●: $[HL] = 5 \times 10^{-3}$ *M*, $[Cu^{2+}] = 1 \times 10^{-3}$ *M*.

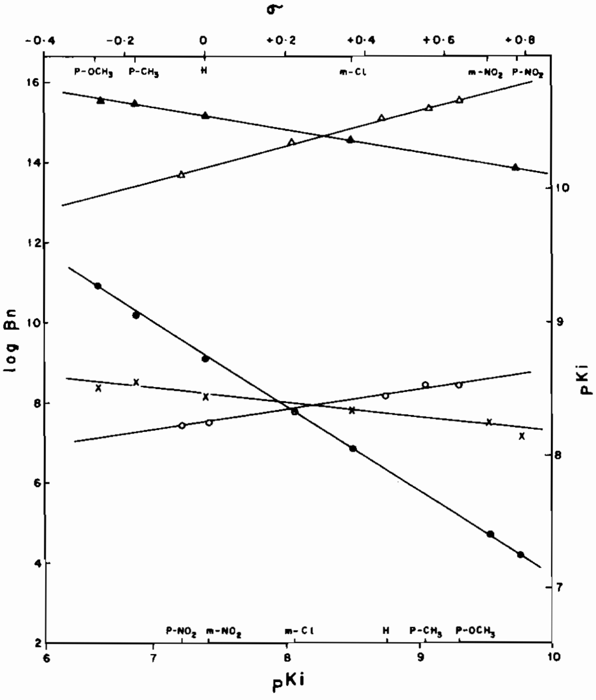

Fig. 2. Correlation of $\log\beta_n$ for copper(II) chelates with pK_i and the Hammett substituent, σ (X: $\log\beta_1$ *vs.* σ; ○: $\log\beta_1$ *vs.* pK_i; ●: pK_i *vs.* σ; ▲: $\log\beta_2$ *vs.* σ; △: $\log\beta_2$ *vs.* pK_i).

The plot of $\bar{n}/(1 - \bar{n})[L^-]$ against $(2 - \bar{n})[L^-]/(1 - \bar{n})$ is a straight line of intercept $\beta_1(K_1)$ and slope $\beta_2(K_1K_2)$. Using the least squares method [7] the computed values are listed in Table I. The values of $\bar{n}$ and L^- were calculated up to precipitation.

Effect of Substituent on Ligand Dissociation

Calculated pK_i values (Table I) show that they depend on the nature of the substituent. The application of Hammett equation to the pK_i values obtained is shown in Fig. 2. Using the least squares method [7] a value of $\rho = -1.91$ was found (correlation coefficient, r = 1). The negative value for ρ indicates that the dissociation of the studied ligands is not facilitated by electron withdrawal. On the other hand, the value of ρ for the dissociation is more than unity (the value of benzoic acid) because the polar effects of substituents are operating on an atom (N) immediately adjacent to the benzene nucleus.

Copper(II) and Nickel(II) Chelates of the Ligands 1a–e

As the relation between Cu(II) and these ligands is regarded as Lewis acid–base reaction, $\log\beta_1$, $\log\beta_2$ is plotted *vs.* pK_i in Fig. 2. This implies that the stability of the chelates is mainly dependent upon the basicity *i.e.* the pK_i value of the ligand. A slope less than unity (0.97) of the linear correlation ($\log\beta_1$ *vs.* pK_i) obtained (Fig. 2) was found as calculated by the least squares method. This result suggests that Cu(II) in complexes studied functions as π-electron donor [9], *i.e.* these chelates were stabilized by back electron donation from the metal ion to the ligand as was suggested for benzoic acids complexes [10]. However, copper chelates with some related series of anilides were stabilized by donation from the ligand [11].

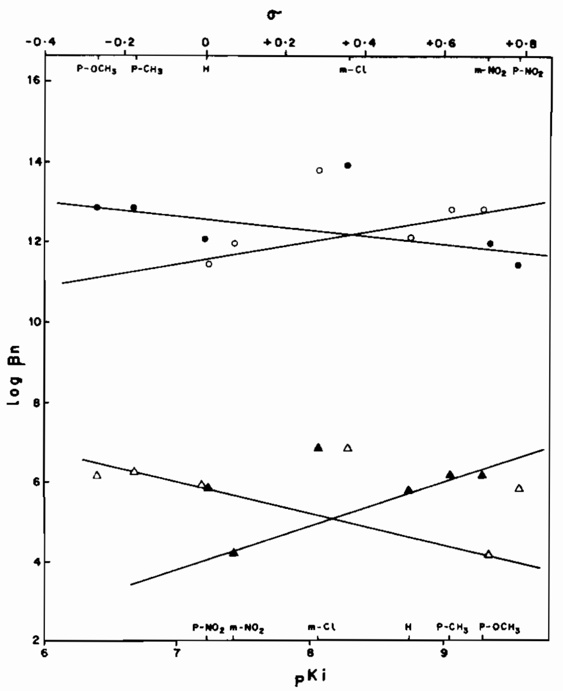

Fig. 3. Relationships between $\log\beta_n$ of nickel(II) chelates with pK_i and the Hammett substituents, σ (△: $\log\beta_1$ *vs.* σ; ▲: $\log\beta_1$ *vs.* pK_i; ●: $\log\beta_2$ *vs.* σ; ○: $\log\beta_2$ *vs.* pK_i).

Figure 3 illustrates the relationships of $\log\beta_1$ and $\log\beta_2$ *vs.* pK_i of the ligands for Ni(II) chelates computed by the previous method (Table I). Although there are some irregularities in the relationship, the stability of the Ni(II) chelates increases with the increase of pK_i, but the nature of bonding may vary from ligand to another especially that in the *meta* positions adjacent to the (–NH–N–) group. Omitting the value of β_2 for the ligand Id, a slope 0.34 which is less than unity is obtained (Fig. 3). Consequently, Ni(II) cations act as π-electron donors [9]. Therefore, the mode of bonding between Cu(II) and Ni(II) and the ligands 1a–1f is identical.

The applicability of Hammett equation to $\log\beta_n$ for Cu(II) and Ni(II) chelates was also examined. It is obvious from Fig. 2 that the equilibrium data of copper show an excellent correlation with the substituent constant, σ. The regression lines of the linear relations obtained can be expressed by the equations:

$$\log\beta_1 = 8.25 - 0.9\sigma, r = 0.98$$

$$\log\beta_2 = 15.13 - 1.8\sigma, r = 0.999$$

Similar correlations were also obtained for Ni(II), Fig. 3, but omitting that of the ligand 1f the regression lines of the linear relationship can be expressed by the equations:

$$\log\beta_1 = 5.929 - 1.07\sigma, r = 0.899$$

$$\log\beta_2 = 12.53 - 1.28\sigma, r = 0.911$$

The question of π-bonding in metal ligand complexes was discussed by many authors. May and Jones [10] reported, contrary to expectation, that the anions of strongest acids formed the strongest complexes. Furthermore they obtained a linear relationship between σ and the stability constants of the complexes. They suggest that although electron-withdrawing substituents tend to weaken the dative, σ, bond between metal and ligand, such substituents enhance the back donation of electrons from copper to ligand. These data of May and Jones are particularly surprising in view of the earlier results [12].

Irving and Dasilva [13] think that S_f, the so called stabilisation factor, is a measure of the stabilisation due to π-bonding. However, Yingest and McDaniel [14] obtained very convincing experimental data. So, according to the obtained linear free energy correlation both Cu(II) and Ni(II) cations act as an π-electron donor, while the data due to the application of Hammett equation, Figs. 4 and 5, indicate the reverse. This may suggest that there is another factor affecting the affinities of these ligands towards chelation such as the steric effect of the bulky groups in the ligands near to the coordination centre, as it causes a steric hindrance to coordination from the carbonyl group to the metal [15], which overcompensates the effect of the increased basicity. Moreover, the chelate resonance may also be interfered by the resonance in the carbonyl group, which will decrease the stability of the chelate [16]. So far by application of Hammett equation we were not able to obtain a definite conclusion about the nature of the π-bonding.

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