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Determination of Stability Constants of Some Substituted 4-Pyrazolone Dyes Containing *o*-Methoxy, *o*-Carboxy, and *o*-Nitro Groups with Trivalent Lanthanide Ions

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The relative stabilities of the metal derivatives of hydrazo pyrazolone dyes containing *ortho* —OCH_3, —COOH, and —NO_2 groups have been measured potentiometrically in 75% (*v*/*v*) dioxane—water mixture at 30 °C and < 0.1 ionic strength. The stability constant of their 1 : 1 and 1 : 2 chelates with twelve trivalent lanthanide ions *Ln*(III) have also been determined. The effects of substituents on the hydrazo-moiety of the ligand on the equilibria are discussed. The affinity of different ligands for complexation with lanthanide ions reaches its highest value with *ortho*-carboxyphenylhydrazopyrazolone. The data were correlated and the results were used to explain the stabilization of such chelates by dative π-bonding between *Ln*(III) and the ligand.

[Keywords: 1-Phenyl-3-methyl-4-(x-phenylhydrazo)-5-pyrazolone ligands; Stability of lanthanide (III)]

Bestimmung der Stabilitätskonstanten einiger o-Methoxy-, o-Carboxy und o-Nitro-substituierter 4-Pyrazolon-Farbstoffe mit trivalenten Lanthanidenionen

Es wurden die relativen Stabilitäten der Metallderivate von Hydrazopyrazolon-Farbstoffen mit *ortho*-O*Me*, —COOH und —NO_2 potentiometrisch in 75% (*v*/*v*) Dioxan—Wasser bei 30 °C und einer Ionenstärke < 0.1 bestimmt. Die Stabilitätskonstanten der 1 : 1 und 1 : 2 Chelate mit zwölf trivalenten Lanthanidenionen *Ln*(III) wurden ebenfalls gemessen. Die Substituenteneffekte werden diskutiert. Dabei zeigen *o*-Carboxyphenylhydrazopyrazolone die höchste Affinität zu Lanthanidenionen. Die Daten werden miteinander korreliert und die Resultate auf der Basis einer dativen π-Bindung zwischen *Ln*(III)-Ion und dem Liganden diskutiert.

Introduction

Questions about the involvement of metal ligand complexes in medical treatment are of special interest [1], especially structure—stability relationships. Pyrazolones were used as analgetics and antipyretics, but their most commercial use was as dyes. *Snavely* et al. [2] determined potentiometrically the relative stabilities of the metal derivatives of simple aryl-azo-5-pyrazolones. The structure stability relationship of some substituted 4-pyrazolone dye chelates with Cu(II) and Ni(II) has recently been reported [3]. In continuation of our studies we have investigated the effect of substituents on the chelating tendency of a series of 5-pyrazolone dyes (I–III) towards a series of lanthanide ions. The hydrazo structure of the ligands (I–III) has been confirmed [4–11].

Experimental

The ligands were prepared by coupling 1-phenyl-3-methyl-5-pyrazolone [12] in sodium acetate with the diazonium salt of the corresponding amine. The crude products were recrystallized from acetic acid.

The purity of the organic ligands were confirmed by chemical analysis and melting points (compare Refs. [12]–[14]); m.p. of (II) 270–271 °C.

The $1.25 \cdot 10^{-2} M$ ligand solutions were prepared by dissolving the accurate weights of ligand in proper volumes of purified dioxane. Stock solutions of the lanthanide were prepared as nitrates from metal oxide (99.9% BDH) as mentioned previously [15] and standard potassium hydroxide was prepared in the usual way.

pH-meter titrations were carried out using a China *pH*-meter Model-25 (reading of $\pm 0.02\,pH$) calibrated by means of standard buffer solutions produced by Burrough's Wellcome & Co. (England). All titrations were carried out in 75% (*v*/*v*) dioxane—water at constant temperature (30 °C) and an inert atmosphere (nitrogen). The *pH*-meter readings were taken after the addition of alkali hydroxide when the reading became constant. The correction for *pH* value in 75% (*v*/*v*) dioxane—water was done using the equation $-\log[\mathrm{H}^+] = pH + 0.28$ [16].

Dioxane was purified following the recommended method [17].

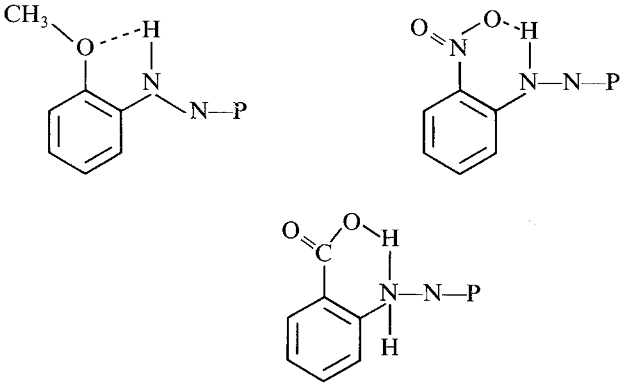
Results and Discussion

The titration curves of 1-phenyl-3-methyl-4-(2-carboxyhydrazo)-5-pyrazolone (II) and 1-phenyl-3-methyl-4-(2-methoxyhydrazo)-5-pyrazolone (I) in presence and absence of Ln^{+3} ion (*Ln* = La, Ce, Pr, Nd... Lu) are illustrated, as examples, in Figs. 1 and 2. The appearance of only one inflection in the titration curve of the free ligand (II) after $m = 1$ (m = number of moles of NaOH added per mole of ligand), corresponds to complete neutralization of the carboxylic proton in a single step. The dissociation of the hydrazo proton on the ligand starts at *pH* 11.0, whereas the appearance of only one weak inflection in the titration curves of the free ligands (I) and (III) after $m = 1$ corresponds to complete neutralization of the hydrazo proton. This inflection is screened in ligand (II) by the sharp inflection of the carboxylic group.

The titration curves of the ligands are greatly altered in presence of *Ln*(III) as a result of the complex formation. The inflection points which occur on the curves of the ligands (I) and (III) at $m = 1$ and on the curves of ligand (II) at $m = 2$ in presence of the lanthanide ion indicate the complete formation of a bis-chelate as the higher complex formed.

The stoichiometric acid dissociation constants *pK* of each ligand are calculated from equations of monoprotic and diprotic acids and the results of the computations are given in Table 1. The calculated values for —NH (Table 1) shows that it depends on the nature of the substituent on the phenylhydrazo moiety (Scheme 1).

Scheme 1



The electron releasing group would make the nitrogen more negative, leading to a higher *pK* for methoxy, while the electron attracting group (—NO_2) would have the opposite effect as seen from its acidity constant. The higher pK_1 value for ligand (II) is due to the chelate formed; after the first ionization a six-membered ring may result from the chelation of the carboxylate oxygen and the hydrazo hydrogen which is less stable than the five-membered chelate ring in ligand (I).

The log K_1 values for *Ln*(III) chelates were calculated using the expression by *Irving* and *Rossotti* [18]:

$$\log\left(\frac{\bar{n}}{1-\bar{n}}\right) = \log K_1 + pL$$

This expression was solved by the graphic relation in the plots of $\log(\bar{n}/1-\bar{n})$ vs. pL. The intersection of the straight line with the pL axis gives the value of $\log K_1$. The values selected of ($\bar{n}$) were between 0.1 and 0.8. The number of readings in each case was 7–8 and all points fell on a straight line whose correlation coefficient was found to be close to unity in each case.

The values of $\log K_2$ were calculated using the equation:

$$\log\left(\frac{\bar{n}-1}{2-\bar{n}}\right) = \log K_2 + pL$$

The values of the selected ($\bar{n}$) were between 1.1 and 1.8. The accurate values of $\log K_1$ and $\log K_2$ were determined by the method of least squares [19]. The linear regression program was used to obtain the best straight line.

The stability constants of the chelates formed are listed in Table 1. In case of ligand (III), $\log K_2$ cannot be determined due to lanthanide precipitation.

The possible hydrolysis of the central ion which can affect the values of the constants appear to be negligible over the experimental range as revealed from data of Lu^{3+}. As the hydrolysis constant of this ion is appreciable, this may lead to the release of protons to the solution which may need some corrections. Supposing that the only species containing Lu^{+3} are $Lu(OH)^{++}$, Lu^{3+}, LuL^{++}, and $LuL_2{}^{+}$, one can calculate $[Lu(OH)^{++}]$ from the experimental points of titration using the calculated values of formation constants K_1 and K_2 and using the equations:

$$K_h = \frac{[Lu(OH)^{++}][H^+]}{[Lu^{3+}]} \quad (K_h = \text{hydrolysis constant})$$

$$\text{and } Lu_T^{3+} = [Lu(OH)^{++}] + [Lu^{3+}] + [LuL^{++}] + [LuL_2^{+}];$$

$$[Lu(OH)^{++}] = \frac{K_h[Lu_T^{3+}]}{K_h + [H^+] + K_1[H^+][L^-] + K_1K_2[H^+][L^-]^2}$$

Using this equation in the pH titration range 4.10–6.03 where $\bar{n}$ reached 1.8 and precipitation does not occur, shows that $[Lu(OH)^{++}]$ is not appreciable compared to $[Lu_T^{3+}]$.

Correlation of Chelate Stability with the Nature of Metal Ion

Figure 3 gives the correlation of $\log K_1$ for phenyl-hydrazo-5-pyrazolone-Ln^{3+} complex with the atomic number of the lanthanide series. A curve is obtained, the first part (La^{+3}—Eu^{+3}) shows linear

Table 1. *Stability constants and free energy (ΔG in kJ mol^{-1}) of lanthanide complexation by 1-phenyl-3-methyl-4(X-phenylhydrazo)-5-pyrazolone ligands*

Metal ion	(I) $X = —2\text{-}OCH_3$ $pK = 12.0 \pm 0.04$				(II) $X = —2\text{-}COOH$ $pK_1 = 7.5 \pm 0.06$; $pK_2 = 11.6 \pm 0.08$				(III) $X = —2\text{-}NO_2$ $pK = 9.7 \pm 0.05$		Ionic potential Z^2/r
	log K_1	ΔG_1	logβ	log(K_1/K_2)	log K_1	ΔG_1	logβ	log(K_1/K_2)	log K_1	ΔG_1	
La^{+3}	7.63	—43.65	14.46	1.12	15.34	—87.75	26.40	1.38	5.76	—32.95	8.48
Ce^{+3}	7.90	—45.19	15.20	1.08	15.53	—88.84	28.57	1.19	6.27	—35.87	8.70
Pr^{+3}	8.14	—46.56	15.37	1.13	15.74	—90.04	29.15	1.17	6.54	—37.41	8.89
Nd^{+3}	8.45	—48.34	15.57	1.19	15.75	—90.09	28.42	1.24	7.03	—40.21	9.05
Sm^{+3}	8.97	—51.31	17.18	1.09	15.85	—90.67	28.81	1.22	7.40	—42.33	9.34
Eu^{+3}	8.80	—50.34	17.12	1.05	15.97	—91.36	28.90	1.23	7.27	—41.59	9.47
Gd^{+3}	8.60	—49.19	16.84	1.04	15.86	—90.73	28.79	1.23	7.38	—42.22	9.60
Tb^{+3}	8.51	—48.68	16.70	1.04	15.80	—90.95	28.50	1.26	7.43	—42.50	9.75
Dy^{+3}	8.46	—48.39	16.43	1.06	15.99	—91.47	28.42	1.28	7.39	—42.27	9.91
Ho^{+3}	8.43	—48.22	16.44	1.05	16.01	—91.58	28.41	1.29	7.45	—42.62	10.07
Er^{+3}	8.39	—47.99	16.49	1.04	16.03	—91.70	28.32	1.30	7.64	43.70	10.22
Yb^{+3}	8.54	—48.85	16.89	1.02	16.18	—92.55	28.02	1.37	7.78	—44.51	10.49
Lu^{+3}	8.70	—49.76	17.13	1.03	16.54	—94.62	30.73	1.17	8.13	—46.51	10.61

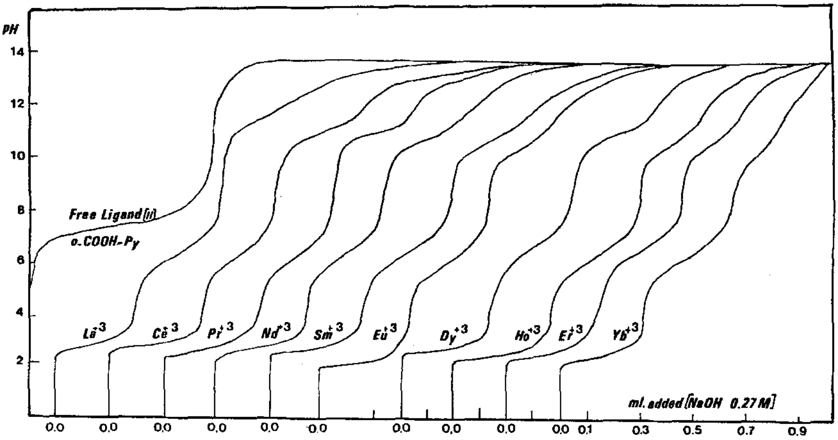


Fig. 1. Potentiometric titration curves for $[5 \cdot 10^{-3} M]$: 1-Phenyl-3-methyl-4-(2-carboxy phenyl hydrazo)-5-pyrazolone in absence and presence of $[1 \cdot 10^{-3} M]$ lanthanide ion ($T = 30$ °C, 75% dioxane—water, $V_0 = 30$ ml)

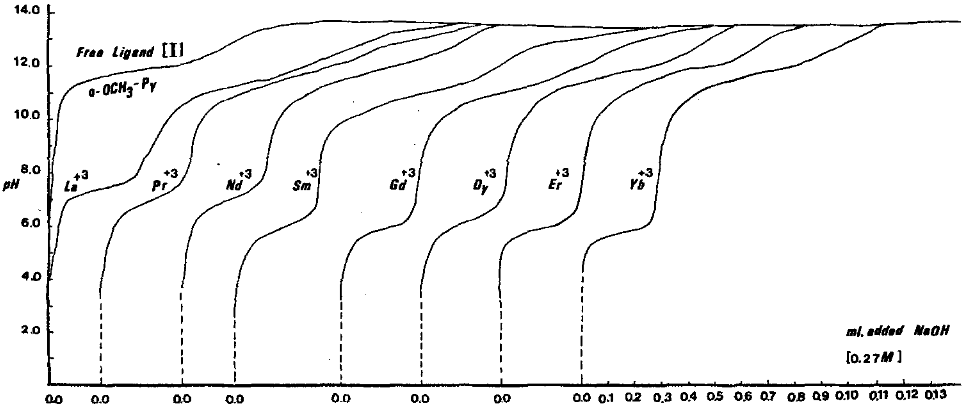


Fig. 2. Potentiometric titration curves for $[5 \cdot 10^{-3} M]$: 1-Phenyl-3-methyl-4-(2-methoxy phenyl hydrazo)-5-pyrazolone in absence and presence of $[1 \cdot 10^{-3} M]$ lanthanide ion ($T = 30$ °C, 75% dioxane—water, $V_0 = 30$ ml)

increase which indicates that in each ligand system the stability of the first complex formed was directly proportional to the total ionization potential of the central metal ion. The second part of the curve (Eu^{+3}—Lu^{+3}) shows a buffer region near the gadolinium area and the stability starts to show a gradual increase from Dy^{+3} to Lu^{+3}. The hydration effect [20–22] can be used for explanation of the variations in the properties of rare earth complexes.

Relation Between log *K and Ionic Radius*

A plot of log K_1 of various lighter rare earth chelates vs. the ionization potentials (Fig. 4) was linear for all the phenyl hydrazo pyrazolone ligands studied in the present work. A similar relationship was obtained with ligands containing nitrogen and oxygen as coordinating sites such as picolinate, N-hydroxy ethylene diamine tetraacetic acid, *EDTA, DCTA* [23–29] and phenyl hydrazo-*β*-diketone [30–33]. In this study, all rare earth ions are in +3 oxidation states and are more or less of the same size. Accordingly, the electrostatic contribution to the metal-ligand bond is assumed to be nearly the same. Therefore, log K_1 values for the lighter metal complexes with different ligands were plotted against the respective overall ionization potentials of Ln^{+3} (Fig. 4) to find the effect of the electron affinity of the rare earth ions on the stability of the complexes they formed.

The Ratio of Successive Stability Constants

As the tendency of the metal ion to coordinate to the azo ligand is proportional to the number of vacant sites, the ratio between consecutive constants is (to a certain extent) statistically determined [34]. Table 1 shows that for all systems studied here, log K_1 — log K_2 is positive and lies within 1.00–1.40 units. The different values of log *K* of the complexes of the studied compounds (I–III) may be explained by the difference in the basicity of these ligands. Calculated values (Table 1) show that they depend on the nature of the substituent on the phenylhydrazo moiety which indicates that the complexation of the studied ligands are not facilitated by electron-withdrawing substituents [35]. The complexation is increased by increasing the electron density at the reaction site. The electron-repelling substituents increase this charge density leading to higher stability, while electron-attracting substituents decrease this charge density leading to less stable complexes [36].

The relatively high values of log K_1 and log K_2 for Ln^{+3}-phenyl hydrazo-5-pyrazolone complexes could be attributed to:

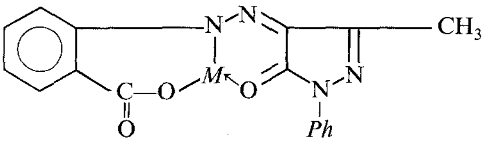
(i) The higher basicity of $pK_1^H + pK_2^H$ of the ligands.

(ii) Different coordinating sites on the ligands as well as the higher coordination number of lanthanides.

(iii) The use of 75% (*v*/*v*) dioxane—water as solvent of low dielectric constant which increases the degree of complexation.

The presence of the carboxylate group at the *ortho*-position leads to participation of this group in chelate formation; this ligand acts as a terdentate as shown in Scheme 2.

Scheme 2



This will lead to the higher stability of its complex. Another factor is that this group is in the same plane and in resonance with the ring leading to greater chelating power of the ligand than the other two.

Although the *o*-NO_2 group can lead to chelate formation we find that the stability of its complexes is the least among these ligands. This may be

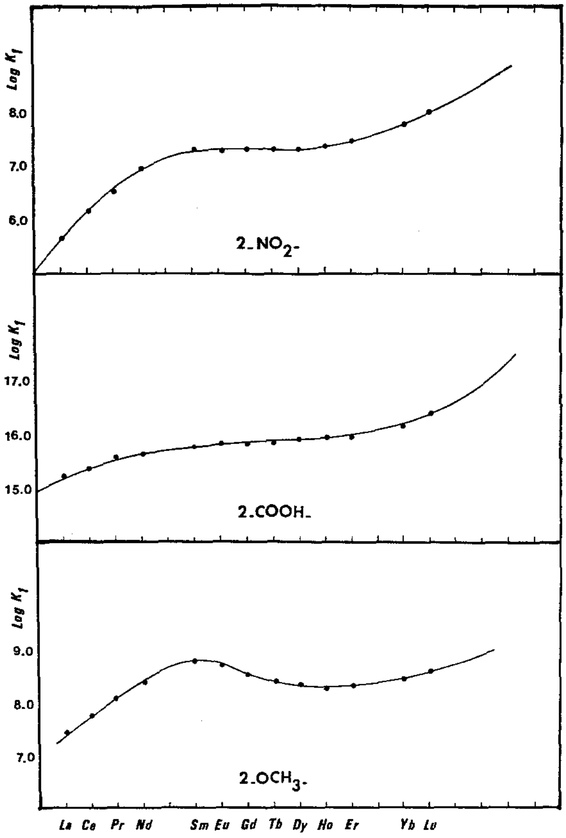


Fig. 3. $\log K_1$ as a function of atomic number for various rare earth complexes

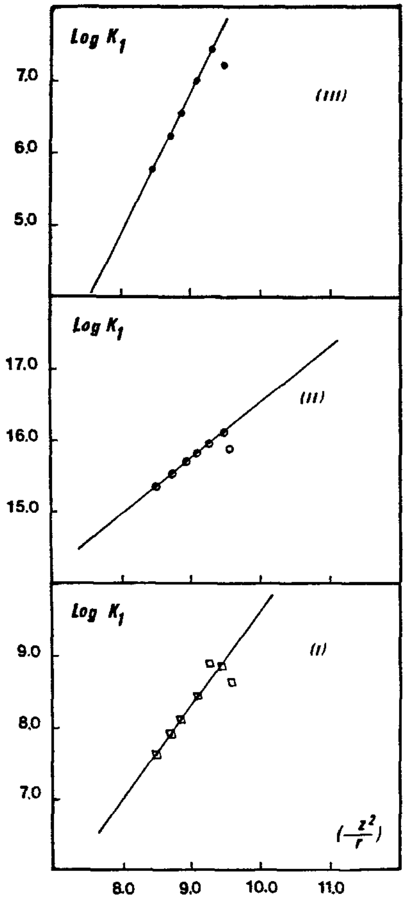


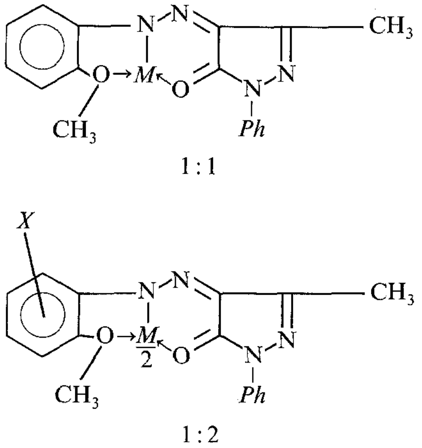
Fig. 4. Correlation of stabilities of rare earth and ionic potentials (z^2/r) for I–III

explained on the basis that the —NO_2 group is a bulky group which favors steric hindrance and distorts the chelate ring from the normal planar structure.

Comparing our results with those reported by other authors [37] for *o*-OCH_3 hydrazopyrazolones showing a strong contribution of the ether oxygen to bond formation, will lead us to the conclusion that *o*-methoxy has a role in the complexation. Under the conditions of these titrations the methyl group of the methoxy does not undergo any hydrolysis in agreement with the work of *Snavely*.

The probable structure of 1 : 1 and 1 : 2 metal : ligand complexes of *o*-CH_3 and *o*-NO_2 hydrazo pyrazolone derivatives can be represented by the structures shown in Scheme 3.

Scheme 3



$M = Ln^{+3}(La^{+3}, Ce^{+3}, Pr^{+3}, Nd^{+3} \ldots\ldots\ldots Lu^{+3})$
$X = o\text{-}OCH_3$ and $o\text{-}NO_2$

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