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Stability Constants of Thorium(IV) Complexes with Aryl-*bis*-(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl) Methane Ligands

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Summary. Stability constants of complexes of aryl-*bis*-(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl) methane [Ar*BPyM*] derivatives with thorium(IV) ions were determined by the potentiometric method at 30°C and an ionic strength of 0.1 mol·dm^{-3} (KNO_3) in 75% (v/v) dioxane-water. The evaluation of the titration data indicated that four kinds of complexes ($[ThL]^{2+}$, $[ThLOH]^{+}$, $[ThL_2]$, and $[ThL(OH)_2]^{2-}$) were formed. The formation constants for all $[ThL]^{2+}$ and $[ThL_2]$ complexes have been calculated to compare these values with those previously reported [1, 2] with Ln^{3+} and UO_2^{2+} metal ions [2, 3]. The probable ligand-bonding sites of the complexes are proposed. In addition, the applicability of the *Hammett* equation for the correlation of the stability constants of [Th(IV)-Ar*BPyM*] complexes are discussed.

Keywords. Thorium complexes; 5-Hydroxy-3-methyl-1-phenyl-4-pyrazolyl methane; Potentiometry; Formation constants.

Stabilitätskonstanten von Thorium(IV)-Komplexen mit Aryl-*bis*-(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl)-methan-Liganden

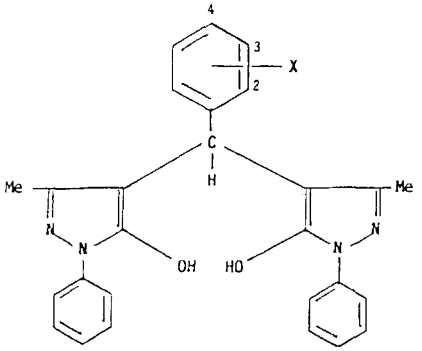
Zusammenfassung. Stabilitätskonstanten von Komplexen von Aryl-*bis*-(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl)-methan – Derivaten [Ar*BPyM*] mit Thorium(IV) – Ionen wurden bei 30°C und einer Ionenstärke von 0.1 mol-dm^{-3} (KNO_3) in 75% (v/v) Dioxan-Wasser potentiometrisch bestimmt. Die Auswertung der Titrationskurven zeigte, daß vier verschiedene Komplexe vorlagen ($[ThL]^{2+}$, $[ThLOH]^{+}$, $[ThL_2]$ und $[ThL(OH)_2]^{2+}$). Die Bildungskonstanten aller $[ThL]^{2+}$- und $[ThL_2]$-Komplexe wurden berechnet, um sie mit den früher für Ln^{3+}- und UO_2^{2+}-Ionen publizierten zu vergleichen. Potentielle Bindungsstellen der Komplexe für Liganden werden vorgeschlagen. Zusätzlich wird die Anwendbarkeit der *Hammet*-Beziehung auf die Korrelation der Stabilitätskonstanten von [Th(IV)-Ar*BPyM*] – Komplexen diskutiert.

Introduction

This paper is an extension of the systematic investigations carried out in the laboratory for studying the metal binding properties of some biocondensation products of aryl-*bis*-(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl) methanes (Ar*BPyM*) [2, 3].

Experimental values of equilibrium constants of metal-ligand complexes are important for the development of coordination chemistry in a number of ways as pointed out by specialists such as *Beck* [3] and Marcus and Eliezer [4]. Acylpyrazolones have been found effective for the efficient extraction of actinides [5, 6]. Similar to acyl pyrazolones, β-diketones derived from 4-acyl and 4-acetyl derivatives of isoxazolones are considered to be attractive as chelating agents for thorium and other metal ions [7, 8]. Thus my objective is to study potentiometrically the interactions of Th(IV) ions with the ligands under investigation and compare the results of the stability constants of the [Th-Ar*BPyM*] complexes with those previously reported concerning (UO_2-Ar*BPyM*] [2]. So, an estimation of the sensitivity and selectivity of these ligands towards the chelation of actinides can be evaluated.

The structures of ligands [1 to 9] are given in Scheme 1.



Scheme 1. Aryl-*bis*-(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl) methane

1: X = H **2**: X = 2-Cl **3**: X = 3-OH
4: X = 3-NO_2 **5**: X = 4-OH **6**: X = 4-$N(Me)_2$
7: X = 4-Cl **8**: X = 2,3,4-$(OMe)_3$ **9**: X = 4-OH, 3-OMe

Experimental

Chemicals

All the chemicals used were of analytical reagent grade (BDH or Merck products).

Peparation of Ligands

The *bis*-condensation products used in this investigation were prepared by adding slowly, with continuous stirring the corresponding substituted aldehyde (30 mmol) dissolved in a minimum quantity of hot ethanol to a solution of 1-phenyl-3-methyl-5-pyrazolone [9] (60 mmol) dissolved in the minimum quantity of the same solvent. The resulting solution was refluxed for 3–4 hours. The product obtained after heating the mixture under reflux was then filtered under suction, washed several times with hot water and hot ethanol and dried over phosphorus pentoxide. The purity of the ligands was confirmed by elemental analyses and their structures were established by IR- and ^1H NMR spectroscopy and *pH*-methods [1].

Potentiometric Titrations

The concentration of the potassium hydroxide solution (0.22 *M*) was determined by titration with potassium hydrogen phthalate (Carlo-Erba).

Thirty cm^3 of a solution of dioxane-water (75% (v/v)) containing 0.005 moles of ligand dissolved in an appropriate volume of purified dioxane and 0.001 moles of metal nitrate was titrated against 0.22 *M* carbonate-free potassium hydroxide. The *pH*-measurements were made with a Radiometer M-26 *pH*-meter (GK 2322) with combined electrodes. During the titrations, the solutions were kept at 30 ± 1 °C and at an ionic strength of 0.1 *M* KNO_3 under a nitrogen atmosphere with continuous stirring.

Calculations

The correction factor for the *pH* value [10, 11] in 75% (v/v) dioxane-water was evaluated using the following equation:

$$\log[\mathrm{H}^+] = pH + 0.28$$

All the dissociation constants were calculated [12] as mentioned before [13], taking into consideration that the value of pK_w in 75% (v/v) dioxane-water was approximately 18.7 [14] and the value of $[\mathrm{OH}^-]$ is very small and may be omitted.

The $\log K_1$ values (stability constant of the first complex formed, $M{:}L = 1{:}1$) for Th(IV) chelates were calculated using the expression by *Irving* and *Rossoti* [15]:

$$\log\frac{\bar{n}}{1-\bar{n}} = \log K_1 + pL$$

The values selected for $\bar{n}$ 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 $\log K_2$ (stability constant of the second complex formed, $M{:}L = 1{:}2$) were calculated using the equation

$$\log\frac{\bar{n}-1}{2-\bar{n}} = \log K_2 + pL$$

The values selected for $\bar{n}$ 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 and a linear regression program was used to obtain the best straight line.

Results and Discussion

Titration Curves

The titration curves of $H_2ArBPyM$ ligands in presence and absence of Th(IV) ions are illustrated in Fig. 1. The reaction of the free ligands at $m = 2$ (m = number of moles of KOH added per mole of ligand) may be represented by equations (1) and (2).

$$\mathrm{H_2Ar}BPyM + \mathrm{OH}^- \overset{K_1^H}{\rightleftharpoons} \mathrm{HAr}BPyM^- + \mathrm{H_2O} \tag{1}$$

$$\mathrm{HAr}BPyM^- + \mathrm{OH}^- \overset{K_2^H}{\rightleftharpoons} \mathrm{Ar}BPyM^{2-} + \mathrm{H_2O} \tag{2}$$

Addition of an equimolar concentration of Th(IV) ions alters the shape of the free ligand titration curve as a result of complex formation and consequently a considerable shift in the position of the end point is observed. The decrease of the initial *pH* value and a buffer region at $m = 0 - 2$ clearly show the displacement of the proton due to complexation. A considerable lowering in the buffer region is

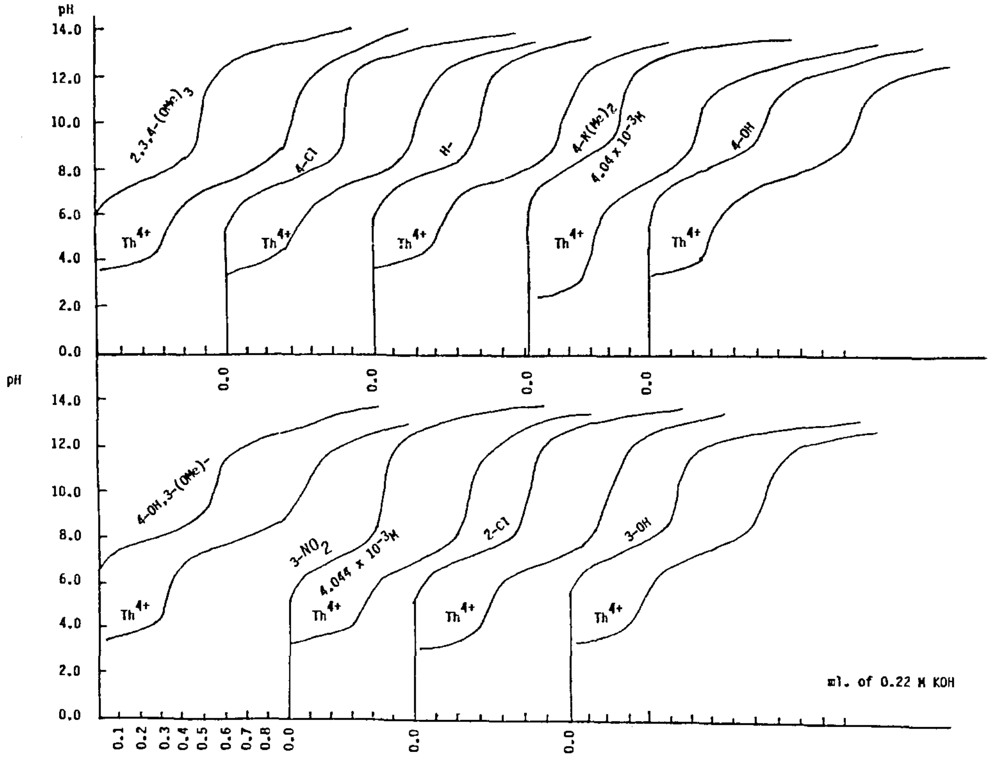


Fig. 1. Potentiometric titration curves for Th^{4+}-aryl-*bis*-(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl) methane complexes. Concentration of ligands: 5×10^{-3} *M*; Concentration of Metal: 1×10^{-3} *M*; T = 30 °C, 75% (v/v) dioxane-water, $V_0 = 30$ ml; 0.1 KNO_3 Aryl substituents as shown on the plot

observed, showing a final inflection at $m = 3$ which suggests the formation of $Th(ArBPyM)^{++}$ and $[Th(ArBPyM)\,(OH)]^+$ complexes. The latter may be associated with the neutralization of a proton from a water molecule coordinated to the metal ion to form a hydroxo metal complex, as usually visualized with the partially chelated metal ion. The formation of $Th(ArBPyM)^{++}$ and $[Th(ArBPyM)\,(OH)]^+$ may be expressed by equations (3) and (4):

$$Th^{4+} + H_2ArBPyM + 2\,OH^- \rightleftharpoons Th(ArBPyM)^{++} + 2\,H_2O \qquad (3)$$

$$Th^{4+} + H_2ArBPyM + 3\,OH^- \rightleftharpoons [Th(ArBPyM)\,(OH)]^+ + 3\,H_2O \qquad (4)$$

The titration of Th(IV) in the presence of two moles of $H_2ArBPyM$ ligand shows an inflection at $m = 3$ which is illustrated above and another inflection after the addition of 6 moles of the base. The latter may be attributed to the formation of $[Th(ArBPyM)_2]$ which consumes 4 moles of base; the other 2 moles of base are responsible for the formation of the dihydroxometal complex $[Th(ArBPyM)\,(OH_2]^{2-}$. The reaction equilibria may be expressed as follows:

$$Th^{4+} + 2\,H_2ArBPyM + 3\,OH^- \rightleftharpoons Th(ArBPyM)^{++} + HArBPyM^- + 3H_2O \qquad (5)$$

$$Th(ArBPyM)^{++} + HArBPyM^- + OH^- \rightleftharpoons Th(ArBPyM)_2 + H_2O \qquad (6)$$

$$Th^{4+} + 2\,H_2ArBPyM + 4\,OH^- \rightleftharpoons Th(ArBPyM)_2 + 4\,H_2O \qquad (7)$$

$$Th^{4+} + H_2ArBPyM + 6\,OH^- \rightleftharpoons [Th(ArBPyM)_2(OH)_2]^{2-} \qquad (8)$$

Table 1. Stability constants of Th^{4+}-aryl-*bis*-(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl) methane complexes at 30 °C and $I = 0.1$ mol·dm^{-3} KNO_3 in 75% (v/v) dioxane-water (aryl substituent as shown in the table)

Aryl Substituent	Protonation constants[a]			$\log K_1$[b]	ΔG[c]	$\log \beta$[d]	[e]$\log K_1/\log K_2$
	[f]pK_1^H	pK_2^H	pK_3^H				
H	7.58(0.01)	12.25(0.03)	–	13.87(0.04)	−79.34	22.95	1.53
2-Cl	7.27(0.03)	12.08(0.02)		13.28(0.02)	−75.97	21.52	1.61
3-OH	7.41(0.01)	11.95(0.02)	12.46(0.01)	13.65(0.02)	−78.08	22.25	1.59
3-NO_2	7.13(0.02)	11.79(0.03)	–	13.22(0.01)	−75.62	20.77	1.75
4-OH	8.85(0.01)	12.07(0.01)	12.69(0.02)	15.07(0.03)	−86.21	25.41	1.46
4-Cl	7.49(0.01)	12.25(0.02)	–	13.85(0.05)	−79.23	22.88	1.53
4-$N(Me)_2$	8.13(0.02)	12.46(0.01)	–	14.90(0.01)	−85.23	24.08	1.62
2,3,4-$(OMe)_3$	7.31(0.03)	12.19(0.02)		13.69(0.01)	−78.31	22.49	1.56
4-OH, 3-(OMe)	7.62(0.01)	10.58(0.01)	12.76(0.03)	12.50(0.05)	−71.51	19.72	1.73

[a] The uncertainty in the protonation constants ranged from ±0.01 to ±0.03 and the correlation coefficient ranged from 0.95 to 0.99.

[b] The uncertainty in the stability constants ranged from ±0.01 to ±0.05 and the correlation coefficient ranged from 0.96 to 0.98.

[c] ΔG_1 in KJ/mol

[d] $\log \beta$: overall stability constants $\log K_1 + \log K_2$

[e] For anionic ligands, the coulombic attraction is stronger for Th^{4+} as compared to ThL; $\log K_1/\log K_2$ is usually positive and lies within 1.46 and 1.75 log units.

[f] Values in parentheses are standard deviations

The formation of these complexes is confirmed by the titration curves (Fig. 1) when the metal to ligand ratio is 1:5.

Correlation between protonation constants of ligands with similar structures and the formation constants of their complexes

Table 1 provides the values of the basicity of the ligands and complex stability constants under the same experimental conditions. It has been pointed out by several workers [16–18] that an approximately linear relationship exists between the logarithms of stability constants of a series of metal complexes derived from one metal ion with the pK^H of a set of closely related ligands. On this basis, it is expected that a more basic ligand should form more stable complexes. The results of the present study show a typical plot for $\log K_1$ *vs.* $\sum pK^H$ for Th(IV)-aryl-*bis*-(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl) methane complexes (Fig. 2). This relation gives a straight line of slope 0.98, whose value indicates the following aspects:

1. The complexation of the Th^{4+} cation increases linearly with the increase of ligand basicity ($\sum pK^H$), which has been attributed to the ionic nature of Th^{4+} [8]. The increase in ligand basicity increases the electronegativity of the coordinating sites of the ligand leading to a strong interaction between the coordinating sites and the Th^{4+} cation, producing a stable chelate.
2. The formation of the same chelate ring upon complexation could be attributed to the similarity of the coordinating sites of the ligands *via* the two enolic oxygens of the two pyrazolyl rings (Scheme 1).
3. The ligands replace the same number of water molecules upon complex formation.

The basis of the correlation between pK_{HL} and K_{MeL} is identical to the nature of the proton – ligand and the metal ion – ligand bonds. If this bond differs in nature, a linear correlation is not to be expected. The most convenient method of plotting and studying the correlation between pK_{HL} and $\log K_{MeL}$ values depends, among other factors, on how many protons the ligand contains in the pH-range of complex formation. The reason why the formation constants for the complexes of (Ar*BPyM*)

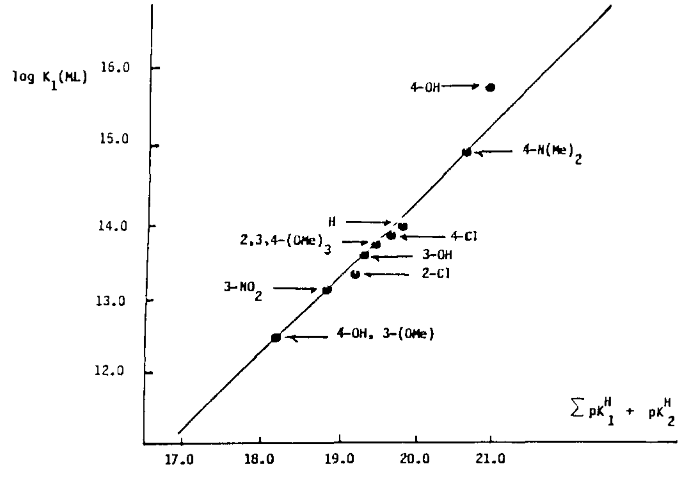


Fig. 2. Linear relationship between $\log K_1$ (ML) and $\sum pK_1^H + pK_2^H$ for Th^{4+}-aryl-*bis*-(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl) methane complexes (aryl substituents as shown in the plot)

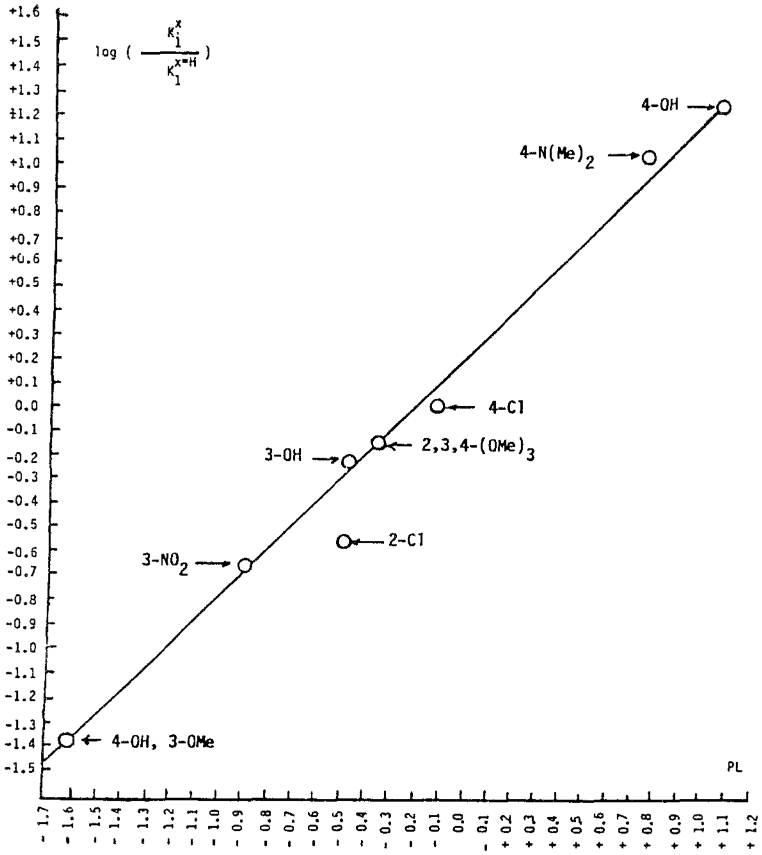


Fig. 3. Relation between P_L constants and $\log(K_1^x/K_1^{x=H})$ for Th^{4+}-ary-*bis*-(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl) methane complexes (arylsubstituent as shown on the plot)

ligands with Th^{4+} as a function of the sum of the two *pK* values is preferred is because both donor groups of the ligand are protonated in the *pH* interval corresponding to the formation of the complexes [19]. The equilibrium process is as follows:

$$Th^{4+} + H_2L \rightleftharpoons [ThL]^{++} + 2\,H^+ \qquad (9)$$

$$Th^{4+} + 2\,H_2L \rightleftharpoons ThL_2 + 4\,H^+ \qquad (10)$$

The statistical correlation of the relation between pK_{HL} and pK_{MeL} follows the equation

$$\log K_1 = 0.968\ pK_{HL} - 5.206 \qquad \text{(Correlation Coefficient} = 0.986)$$

Using the resulting dissociation constants for Ar*BPyM* ligands and taking that of $[H{\cdot}C_6H_4{-}C{<}(Py)_2]$ (where $H{\cdot}C_6H_4{-}C{<}$ = benzyl moiety, Py = 1-phenyl-3-methyl-5-pyrazolone) as the parent substance, one can obtain the values of the ligand constant P_L (the change in the protonation constant induced by replacement of the hydrogen atom of the benzyl moiety by the substituent X). On plotting $\log(K_1^x/K_1^{x=H})$ *vs.* these P_L values (Fig. 3), a straight line was obtained with a positive slope of 0.95, indicating that the reaction is increased by increasing electron density at the reaction site. Electron repelling substituents increase this charge density

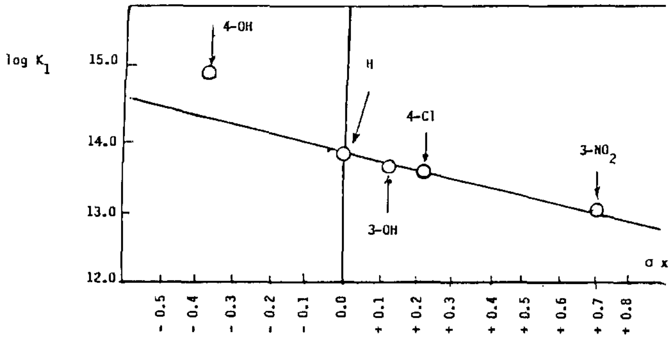


Fig. 4. Plot of *Hammett* σ-constants *vs.* $\log K_1$ for Th^{4+}-aryl-*bis*-(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl) methane complexes (aryl substituent as shown on the plot)

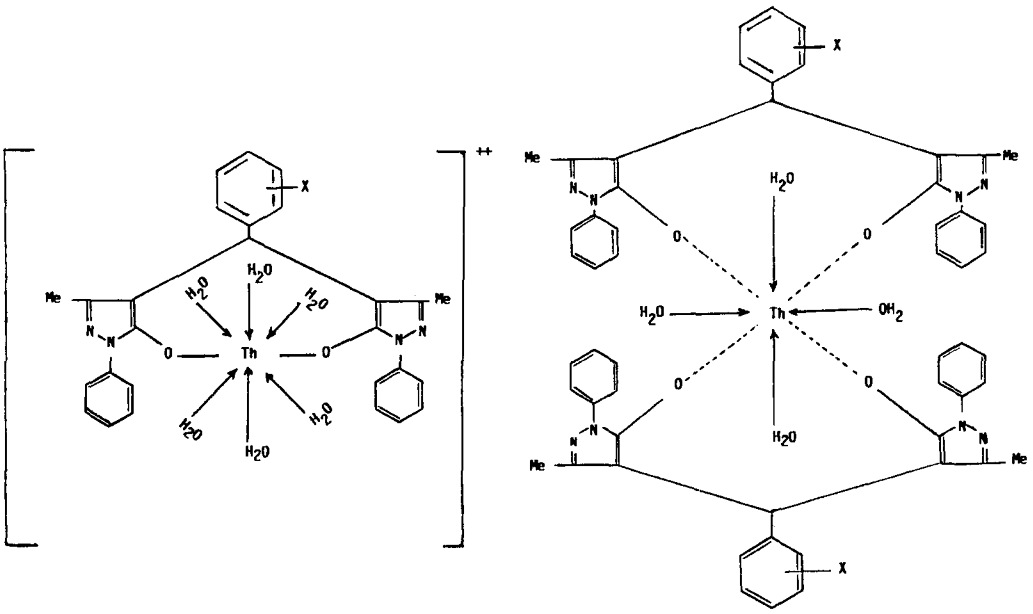
leading to higher stability, while electron attracting substituents decrease this charge density, thus yielding less stable complexes.

Applicability of the Hammett equation

A plot of *Hammett* σ-constants against $\log K_1$ for Th^{4+}-Ar*BPyM* complexes (Fig. 4) gave a straight line with a negative slope, indicating that the stability of the complexes depends on the nature of the substituent on the benzyl moiety. Thus, it is expected that a more basic ligand should form more stable complexes.

Comparing the results obtained in the previous paper [2] concerning the stability constants of UO_2^{2+} with the same ligands, one can conclude that Th^{4+} forms stronger complexes than UO_2^{2+} which has been attributed to its higher effective charge.

From the foregoing results, the mode of coordination of the Th^{4+} ion with the ligands in 1:1 and 1:2 metal ligand ratios can be represented by structures I and II (Scheme 2).



1 : 1
(I)

1 : 2
(II)

Scheme 2. Structures of 1:1 and 1:2 ratios for Th(IV)-Ar*BPyM* complexes

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