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Effect of the Varying π-Accepting Properties of Some *ortho*-Substituted Benzoic Acids on the Stability of Mixed-Ligand Complexes also Containing Quinizarin and Thorium(IV)

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The mixed-ligand complexes of thorium(IV) with quinizarin (*quin*) and as a second ligand, *L*, salicyclic acid (*sa*), thiosalicylic acid (*tsa*) or anthranilic acid (*ant*) were studied potentiometrically in 40% (*v*/*v*) ethanol-water medium [$I = 100\,\text{mmol dm}^{-3}$ (KNO_3), 25 ± 0.1 °C]. The equilibria existing in solutions were demonstrated and the ternary stability constants of the 1:1:1 Th-*quin*-*L* complexes were characterized. All of these biligand complexes are considerably more stable than the corresponding monoligand ones. In addition, the relatively most stable ternary complex is formed with *ant* which is the best π-acceptor. The order of stability of the ternary complexes is in accordance with the calculated π-charge densities of the varying ligating group in the ligand *L*. The values of the equilibrium constants (log units) for the reaction: $\mathrm{Th}(quin)_2 + \mathrm{Th}L_2 \rightleftharpoons 2\,\mathrm{Th}(quin)(L)$ are 2.47 (0.13), 2.60 (0.3) and 4.25 (0.86) for Th(*quin*)(*tsa*), Th(*quin*)(*sa*) and Th(*quin*)(*ant*), respectively. The constants given in parentheses correspond to $\Delta \log K_{\mathrm{Th}} (= \log K^{\mathrm{Th}(quin)}_{\mathrm{Th}(quin)(L)} - \log K^{\mathrm{Th}}_{\mathrm{Th}L})$.

(Keywords: Thorium(IV) mixed-ligand complexes; Stability constants; Quinizarin)

Der Effekt verschiedener π-Acceptoreigenschaften einiger ortho-substituierter Benzoesäuren auf die Stabilität von Komplexen mit gemischten Liganden unter Beteiligung von Chinizarin und Thorium(IV)

Die gemischtligandigen Komplexe von Thorium(IV) mit Chinizarin (*quin*) und als zweiten Liganden (*L*) Salizylsäure (*sa*), Thisalizylsäure (*tsa*) oder Anthranilsäure (*ant*) wurden potentiometrisch in 40% (*v*/*v*) Ethanol-Wasser [$I = 100\,\text{mmol dm}^{-3}$ (KNO_3), $t = 25 \pm 0.1$ °C] untersucht. Die vorliegenden Gleichgewichte wurden formuliert und die ternären Stabilitätskonstanten der 1:1:1 Th-*quin*-*L*-Komplexe bestimmt. Alle zweiligandigen Komplexe sind wesentlich stabiler als die entsprechenden Monoligand-Komplexe. Der relativ stabilste Komplex wurde mit *ant* gebildet, da *ant* der beste π-Acceptor ist. Die Reihung der relativen Stabilitäten stimmt mit den berechneten π-Elektronendichten der verschiedenen Liganden L überein. Die Werte der Gleichgewichtskonstanten (in log Einheiten) für die Reaktion $\mathrm{Th}(quin)_2 + \mathrm{Th}L_2 \rightleftharpoons 2\,\mathrm{Th}(quin)(L)$ sind 2.47 (0.13), 2.60 (0.30) and 4.25 (0.86) für Th(*quin*)(*tsa*), Th(*quin*)(*sa*) bzw. Th(*quin*)(*ant*), wobei die Werte in Klammern $\Delta \log K_{\mathrm{Th}} = \log K^{\mathrm{Th}(quin)}_{\mathrm{Th}(quin)(L)} - \log K^{\mathrm{Th}}_{\mathrm{Th}L}$ entsprechen.

Introduction

Several studies have been reported on the mixed-ligand complexes of Th(IV). The ternary complexes of thorium with *EDTA* and various amino acids [1], nucleosides, purines or pyrimidines [2] as secondary ligands were investigated potentiometrically.

Complex formation between the 1:1 Th-*EDTA* complex and diphenic acid [3], gallic acid [4], glycolic acid and malic acid [5] was also examined. The use of triaminopentacetic acid [6] (*DTPA*) or nitrilotriacetic acid [7] as a primary ligand in ternary complex formation of Th(IV) has also been investigated.

In connection with our continuing research on ternary complex formation involving an acid anthraquinone dye [8–13], we have studied the ternary complexes formed between the 1:1 Th(IV)-*quin* complex and an *ortho*-hydroxy, mercapto- or aminobenzoic acid. This study was undertaken to explore the potentialities of *quin* in ternary complex formation and also the effect of the varying π-accepting capability of the secondary ligands used on the stability of the ternary complexes of Th(IV). The various equilibria existing in solutions were formulated and the stability of the different ternary complexes were characterized. The *Irving* and *Rossotti pH*-titration technique [14] and its modifications [15, 16] were employed. Measurements were made at 25 ± 0.1 °C and $I = 100$ mmol dm^{-3} (KNO_3) in 40% (*v*/*v*) ethanol. In this work, a decisive insight is given about the stability increasing properties of the ternary complexes under investigation by using SCF-MO molecular orbital calculations of the π-charge densities of the chelating sites of the secondary ligands. These calculations were carried out using the *Pariser-Parr-Pople* (*PPP*) approximation [17] in addition to that of *Nishimoto* and *Forster* [18].

Experimental

Analytical-grade reagents and deionized water (or pure ethanol) were used for preparation of solutions: 10^{-3} mol dm^{-3} stock solutions of *quin, sa, tsa*, and *ant* were prepared by dissolving the accurately weighed amount of the reagent in ethanol. A solution of Th(IV) ($5 \cdot 10^{-3}$ mol dm^{-3}) was prepared using AnalaR thorium nitrate and standardized as recommended. Standard solutions of NaOH (0.1 mol dm^{-3}) and HNO_3 ($2.5 \cdot 10^{-2}$ mol dm^{-3}) were also prepared. More dilute solutions of the reagents were obtained as required by accurate dilution.

The *pH*-titrations were carried out at 25 ± 0.1 °C using an Orion (M 601 A) digital *pH*-meter with a combined electrode. Measurements were performed in 40% (*v*/*v*) ethanol-water medium. Correction of *pH* readings in this medium was made as given elsewhere [19]. The ionic strength of solutions was kept constant at 100 mmol cm^{-3} (KNO_3). Data processing calculations were done on a Casio FP-200 computer.

Dissociation Constants of the Ligands and Stability Constants of the Binary and Ternary Complexes

The acid-base properties of quin in water-organic solvent mixtures have been discussed previously [20]. The predominate form of this reagent in solutions of *pH* 3–8 is the neutral species (H_2A) which undergoes stepwise ionisation on increasing the *pH* of the solution. In this work the dissociation constants $pK^{H}_{H_2A}$ and pK^{H}_{HA} of *quin* in 40% (*v*/*v*) ethanol were determined by potentiometric titration of 50 cm^3 of $2.5 \cdot 10^{-3}$ mol dm^{-3} HNO_3 and KNO_3 (I = 100 mmol dm^{-3}) in the presence and absence of the ligand (10^{-4} mol dm^{-3}) with standard carbonate-free NaOH ($1.05 \cdot 10^{-2}$ mol dm^{-3}). The dissociation constants ($pK^{H}_{H_2L}$ and or pK^{H}_{HL}) of *sa*, *tsa*, and *ant* were also determined under the same experimental conditions. The values of the acid dissociation constants of *quin* and the secondary ligands investigated, as depicted from the titration graphs, are given in Table 1. The stability constants of the binary complexes were computed from the titration curves in which the metal-ligand ratio was 1:2. The conditions for measurements were the same as for the acidity constants. Titration of solutions without ligand were used as a basis for the evaluation. The conditions of measurements for the titrations of the ternary complex were the same as for the binary ones, but the solutions contained equivalent amounts of *quin* and Th(IV) and *L*. The evaluation of the titration curves was done using the same solutions but without *L*. Multiple titrations were carried out for each system. The uncertainties given in Tables 1 and 2 are three times the standard deviation.

For the following equilibria in binary systems containing *quin*:

$$\mathrm{Th} + quin \overset{K^{\mathrm{Th}}_{\mathrm{Th}(quin)}}{\rightleftharpoons} \mathrm{Th}(quin) \qquad (1)$$

$$\mathrm{Th}(quin) + quin \overset{K^{\mathrm{Th}(quin)}_{\mathrm{Th}(quin)_2}}{\rightleftharpoons} \mathrm{Th}(quin)_2 \qquad (2)$$

the formation constants were calculated taking into account the species H, H_2A, H*A*, Th, Th(H*A*), and Th(H*A*)$_2$ where H_2A is the neutral form of *quin*.

The overall stability constant for the complexation equilibrium

$$\mathrm{Th} + quin + L \rightleftharpoons \mathrm{Th}(quin)(L),\ \beta^{\mathrm{Th}}_{\mathrm{Th}(quin)L} \qquad (3)$$

was calculated by considering the species H, H_2A, H*A*, H_2L, H*L*, *L*, Th, Th*L*, ThL_2, Th(H*A*), Th(H*A*)$_2$, and Th(H*A*)*L* where H*L* represents the monoanionic form of the secondary ligands *sa* or *tsa*, or alternatively the neutral form of *ant*. The stepwise formation constants for equilibria in Eqs. (2) and (4) were calculated, considering the relevant data or the acid dissociation constants and the comulative binary and ternary constants

$$\mathrm{Th}(quin) + L \rightleftharpoons \mathrm{Th}(quin)L,\ K^{\mathrm{Th}(quin)}_{\mathrm{Th}(quin)L} \qquad (4)$$

Table 1. *Negative logarithms of the acidity constants of the ligands in 40% (v/v) ethanol*

Ligand (L)	$pK^{H}_{H_2L}$	pK^{H}_{HL}
sa	3.15 ± 0.04	13.86[a]
tsa	4.30 ± 0.01	9.15 ± 0.02
ant	—	6.50 ± 0.03
quin	9.55 ± 0.02	11.05 ± 0.03

[a] Ref. [24]

Results and Discussion

The potentiometric titration graph for *quin* in the neutral form (H_2A) shows two inflections at $a = 1$ and $a = 2$ (a = mol of base added per mol of ligand). The constants $pK^{H}_{H_2A}$ and pK^{H}_{HA} corresponding to the stepwise dissociation of the ligand are given in Table 1. The titration graph for a system containing 1:2 molar ratio of Th(IV) and *quin* exhibits two inflections at $m = 1$ and $m = 2$ (m = mol of base added per mol of metal ion) indicating the formation of mono- and bis binary complexes, the corresponding equilibria may be represented as follows

$$\mathrm{Th}^{4+} + \mathrm{H}_2A \rightleftharpoons [\mathrm{Th(H}A)]^{3+} + \mathrm{H}^+,\ K^{\mathrm{Th}}_{\mathrm{Th}(quin)} \tag{5}$$

$$[\mathrm{Th(H}A)]^{3+} + \mathrm{H}_2A \rightleftharpoons [\mathrm{Th(H}A)_2]^{2+} + \mathrm{H}^+,\ K^{\mathrm{Th}(quin)}_{\mathrm{Th}(quin)_2} \tag{6}$$

For the secondary ligands H_2L (*sa*, *tsa*) or HL (*ant*) and their binary complexes with Th(IV), the constants corresponding to the following equilibria were calculated (Table 2).

Th(IV)-*tsa* complexes:

$$\mathrm{Th}^{4+} + \mathrm{H}_2L \rightleftharpoons [\mathrm{Th}L]^{2+} + 2\,\mathrm{H}^+,\ K^{\mathrm{Th}}_{\mathrm{Th}(tsa)} \tag{7}$$

$$[\mathrm{Th}L]^{2+} + \mathrm{H}_2L \rightleftharpoons \mathrm{Th}(L)_2 + 2\,\mathrm{H}^+,\ K^{\mathrm{Th}(tsa)}_{\mathrm{Th}(tsa)_2} \tag{8}$$

$$\mathrm{Th}^{4+} + 2\,\mathrm{H}_2L \rightleftharpoons \mathrm{Th}L_2 + 4\,\mathrm{H}^+,\ \beta^{\mathrm{Th}}_{\mathrm{Th}(tsa)_2} \tag{9}$$

Th(IV)-*sa* complexes:

$$\mathrm{Th}^{4+} + \mathrm{H}L^- \rightleftharpoons [\mathrm{Th}L]^{2+} + \mathrm{H}^+,\ K^{\mathrm{Th}}_{\mathrm{Th}(sa)} \tag{10}$$

$$[\mathrm{Th}L]^{2+} + \mathrm{H}L^{-} \rightleftharpoons \mathrm{Th}(L)_2 + \mathrm{H}^{+}, \quad K^{\mathrm{Th}(sa)}_{\mathrm{Th}(sa)_2} \tag{11}$$

$$\mathrm{Th}^{4+} + 2\,\mathrm{H}L^{-} \rightleftharpoons \mathrm{Th}(L)_2 + 2\,\mathrm{H}^{+}, \quad \beta^{\mathrm{Th}}_{\mathrm{Th}(sa)_2} \tag{12}$$

Th(IV)-*ant* complexes:

$$\mathrm{Th}^{4+} + \mathrm{H}L \rightleftharpoons [\mathrm{Th}L]^{3+} + \mathrm{H}^{+}, \quad K^{\mathrm{Th}}_{\mathrm{Th}(ant)} \tag{13}$$

$$[\mathrm{Th}L]^{3+} + \mathrm{H}L \rightleftharpoons [\mathrm{Th}(L)_2]^{2+} + \mathrm{H}^{+}, \quad K^{\mathrm{Th}(ant)}_{\mathrm{Th}(ant)_2} \tag{14}$$

$$\mathrm{Th}^{4+} + 2\,\mathrm{H}L \rightleftharpoons [\mathrm{Th}(L)_2]^{2+} + 2\,\mathrm{H}^{+}, \quad \beta^{\mathrm{Th}}_{\mathrm{Th}(ant)_2} \tag{15}$$

Table 2. *Logarithms of the stability constants of the binary Th(IV) complexes* [$I = 0.1$; 25 ± 0.1 °C, 40% (v/v) ethanol]

Ligand (L)	$\log K^{\mathrm{Th}}_{\mathrm{Th}L}$	$\log K^{\mathrm{Th}}_{\mathrm{Th}L_2}$	$\log \beta^{\mathrm{Th}}_{\mathrm{Th}L_2}$
quin	6.26 ± 0.04	4.27	10.53
sa	4.41 ± 0.01	3.74	8.22
tsa	4.45 ± 0.03	3.90	8.35
ant	4.80 ± 0.02	4.26	9.06

The potentiometric titration graphs for ternary systems containing Th(IV), *quin* and *sa* or *ant* in a 1:1:1 molar ratio exhibit a single steep inflection at $m = 2$ (Fig. 1). In the ternary system involving *tsa* as the secondary ligand an inflection is obtained at $m = 3$.

The overall stability constant β (Eq. 3) which was determined experimentally, is connected with $K^{\mathrm{Th}(L)}_{\mathrm{Th}(quin)L}$ and $K^{\mathrm{Th}(quin)}_{\mathrm{Th}(quin)L}$ by Eqs. (16) and (17).

$$\log K^{\mathrm{Th}L}_{\mathrm{Th}(quin)L} = \log \beta^{\mathrm{Th}}_{\mathrm{Th}(quin)L} - \log K^{\mathrm{Th}}_{\mathrm{Th}L} \tag{16}$$

$$\log K^{\mathrm{Th}(quin)}_{\mathrm{Th}(quin)L} = \log \beta^{\mathrm{Th}}_{\mathrm{Th}(quin)L} - \log K^{\mathrm{Th}}_{\mathrm{Th}(quin)} \tag{17}$$

In order to quantify the stability of the mixed-ligand complexes we evaluate two parameters: one is based on the difference of stability constants, $\Delta \log K_{\mathrm{Th}}$, (Eqs. 1, 4, 18, and 19) and the other on the "disproportionation" constant $\log X$ (Eqs. 20 and 21).

$$\mathrm{Th} + L \rightleftharpoons \mathrm{Th}L \tag{18}$$

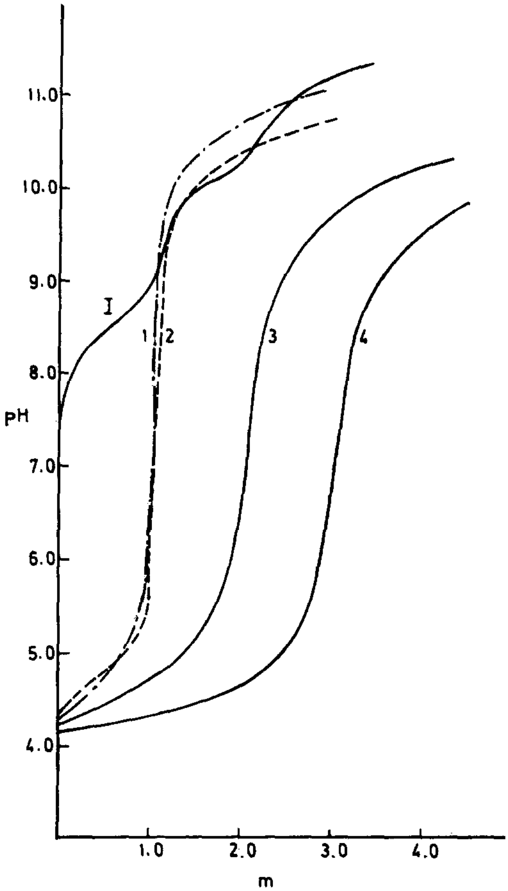


Fig. 1. Potentiometric titration curves of binary and ternary complex systems of thorium(IV) [$I = 0.1 M$ KNO_3; 40% (v/v) ethanol], for *I* the abscissa represents the moles of alkali added per mole of ligand (a); *I quin*; *1* 1:1 Th(IV): *quin*; *2* 1:1 Th(IV): *ant*; *3* 1:1:1 Th(IV): *quin*: *ant*; *4* 1:1:1 Th(IV): *quin*: *tsa*

$$\begin{aligned}\Delta \log K_{\mathrm{Th}} &= [\log K^{\mathrm{Th}(quin)}_{\mathrm{Th}(quin)L} - \log K^{\mathrm{Th}}_{\mathrm{Th}L}] \\ &= [\log K^{\mathrm{Th}L}_{\mathrm{Th}L(quin)} - \log K^{\mathrm{Th}}_{\mathrm{Th}(quin)}] \qquad (19)\end{aligned}$$

$$\mathrm{Th}(quin)_2 + \mathrm{Th}L_2 = 2\,\mathrm{Th}(quin)(L) \qquad (20)$$

$$\log X = 2 \log \beta^{\mathrm{Th}}_{\mathrm{Th}(quin)L} - [\log \beta^{\mathrm{Th}}_{\mathrm{Th}(quin)_2} + \log \beta^{\mathrm{Th}}_{\mathrm{Th}L_2}] \qquad (21)$$

The value of $\Delta \log K_{\mathrm{Th}}$ is the logarithm of the equilibrium constant due to Eq. (22).

$$\mathrm{Th}(quin) + \mathrm{Th}L \rightleftharpoons \mathrm{Th}(quin)L + \mathrm{Th} \qquad (22)$$

In general, negative values for $\Delta \log K_{\mathrm{Th}}$ (Eq. 19) are expected. The statistical values obtained for the coordination of two different bidentate ligands to a regular and to a distorted octahedral coordination sphere are -0.4 and -0.9 respectively [21].

The statistical values for $\log X$ is for all geometries of the coordination sphere of a metal ion the same and is 0.6 [22, 23].

Comparing the curves resulting from the titration of Th(IV) and the secondary ligands L in a molar ratio of 1:1 with that where, in addition, *quin* was present (ratio 1:1:1) one can observe that the deprotonation of *quin* in the ternary systems occurs at lower *pH*. This means that the ternary complexes are more stable than the corresponding binary systems and we shall obtain positive $\Delta \log K$ value in all these instances.

Generally, the experimental data show that the formation of the ternary complexes shifts the buffer region of the ligand to lower *pH* values, which indicate that all the ternary complexes are more stable than the binary complex.

According to our results, the complex equilibria for the Th(IV)-*quin*-L ternary complexes can be represented by the following schemes:

Th(IV)-*quin*-*tsa* ternary system:

$$\mathrm{Th}^{4+} + \mathrm{H}_2A + \mathrm{H}_2L \rightleftharpoons [\mathrm{Th(H}A)L]^{+} + 3\,\mathrm{H}^{+},\ \beta^{\mathrm{Th}}_{\mathrm{Th}(quin)L} \qquad (23)$$

$$[\mathrm{Th(H}A)]^{3+} + \mathrm{H}_2L \rightleftharpoons [\mathrm{Th(H}A)L]^{+} + 2\,\mathrm{H}^{+},\ K^{\mathrm{Th}(quin)}_{\mathrm{Th}(quin)L} \qquad (24)$$

$$[\mathrm{Th(H}A)_2]^{2+} + \mathrm{Th}L_2 \rightleftharpoons 2\,[\mathrm{Th(H}A)L]^{+},\ X \qquad (25)$$

Th(IV)-*quin*-*sa* ternary system:

$$\mathrm{Th}^{4+} + \mathrm{H}_2A + \mathrm{H}L^{-} \rightleftharpoons [\mathrm{Th(H}A)L]^{+} + 2\,\mathrm{H}^{+},\ \beta^{\mathrm{Th}}_{\mathrm{Th}(quin)L} \qquad (26)$$

$$[\mathrm{Th(H}A)]^{3+} + \mathrm{H}L^{-} \rightleftharpoons [\mathrm{Th(H}A)L]^{+} + \mathrm{H}^{+},\ K^{\mathrm{Th}(quin)}_{\mathrm{Th}(quin)L} \qquad (27)$$

$$[\mathrm{Th(H}A)_2]^{2+} + \mathrm{Th}L_2 \rightleftharpoons 2\,[\mathrm{Th(H}A)L]^{+},\ X \qquad (28)$$

Th(IV)-*quin*-*ant* ternary system:

$$\mathrm{Th}^{4+} + \mathrm{H}_2A + \mathrm{H}L \rightleftharpoons [\mathrm{Th(H}A)L]^{2+} + 2\,\mathrm{H}^{+},\ \beta^{\mathrm{Th}}_{\mathrm{Th}(quin)L} \qquad (29)$$

$$[\mathrm{Th(H}A)]^{3+} + \mathrm{H}L \rightleftharpoons [\mathrm{Th(H}A)L]^{2+} + \mathrm{H}^{+},\ K^{\mathrm{Th}(quin)}_{\mathrm{Th}(quin)L} \qquad (30)$$

$$[\mathrm{Th(H}A)_2]^{2+} + [\mathrm{Th}L_2]^{2+} \rightleftharpoons 2\,[\mathrm{Th(H}A)L]^{2+},\ X \qquad (31)$$

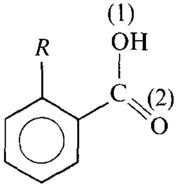
Table 3. *Logarithms of the equilibrium constants of Th(IV) ternary complexes and some related data*
[$I = 0.1$; 25 ± 0.1 °C, 40% (v/v) ethanol]

Ligand (L)	$\log \beta^{\mathrm{Th}^{a}}_{\mathrm{Th}(quin)(L)}$	$\log K^{\mathrm{Th}(quin)^{b}}_{\mathrm{Th}(quin)(L)}$	$\log K_{\mathrm{Th}}{}^{c}$	$\log X^{d}$
sa	10.61 ± 0.02	4.35	− 0.13	2.47
tsa	10.74 ± 0.04	4.48	− 0.03	2.60
an	11.92 ± 0.05	5.66	0.86	4.25

[a] Eq. (3) [c] Eq. (19)
[b] Eq. (17) [d] Eq. (21)

The results obtained for the formation of Th(IV)-*quin-L* ternary complexes are given in Table 3. The values of $\Delta \log K_{\mathrm{Th}}$ (Eq. 19) and $\log X$ (Eq. 21) indicate that, in the presence of *quin*, thorium(IV) prefers to interact with *ant*. This means that the Th(*quin*) complex exhibits discriminatory qualities: it prefers to coordinate with the *ortho*-aminobenzoic acid, rather than with the sulphydryl or the hydroxy analogues. The stability of the ternary complexes increases within the following series of ligands: *tsa* < *sa* < *ant*. The observed difference in stabilities of these ternary complexes can solely be attributed to the varying π-accepting properties of the three secondary ligands.

Table 4. *Values of π-charge densities of donor centers for ligands L*



	tsa	*sa*	*ant*
R (donor atom)	+ 0.00011	+ 0.01093	+ 0.05730
(1)	+ 0.01707	+ 0.01760	+ 0.0240
(2)	− 0.260	− 0.260	− 0.290

The results of SCF-MO calculations indicate that the above order of stability is in accordance with the increase of the π-charge densities ($\delta +$) of the different binding sites in the three *ortho*-substituted benzoic acids. This demonstrates that the π-acceptor properties of the latter are crucial for the enhanced stability of the ternary complexes.

The computed values of the π-charge densities ($\delta +$) of the donor centers of the ligand L (using molecular orbital calculations) are given in Table 4.

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