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Thermodynamics of complexation of lanthanides by some benzoic acid derivatives in aqueous solution

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Abstract

The thermodynamic parameters of formation of 1 : 1 complexes between lanthanide cations and some benzoic acid derivatives were determined by potentiometric and calorimetric titration methods in aqueous solution. The benzoic acid derivatives studied were 4-aminobenzoate, 4-hydoxybenzoate, and 4-nitrobenzoate. All complexation measurements were made at 25°C in an aqueous medium of ionic strength 0.1 M $NaClO_4$. The thermodynamic parameters for the complexation are discussed in relation to the electronic effect of the substituent groups within the ligands. It has been found that the stabilities of the complexes are affected by the nature of the *para*-substituted group in the phenyl ring of the carboxylate ligands. Theoretical calculations of the charge distributions on the carbon atoms of various substituted benzoate ligands were also performed. It was found that the stability constants of the complexes increase with increasing negative charge shifts of carboxylate carbon atoms of substituted benzoate ligands in changing from the ionized form to the metal-complexed form.

Keywords: Charge density; Complexation; Substituted benzoate; Lanthanon; Stability; Thermodynamics

1. Introduction

The complexation of trivalent lanthanide cations with various carboxylates in aqueous solution has been extensively studied [1,2]. In the complexation studies of lanthanides by various aromatic monocarboxylate ligands [1,3,4], it has been found that the stability constants of the complexes correlate well with the acidity constants of the ligands, as also for the aliphatic monocarboxylate complexes [4,5]. For the complexes of the ligands which have such strong electron-withdrawing substituents such as F and NO_2 on the benzene ring, there seems to be no charge polarization via resonance effects by the lanthanide cations [4]. However, the stabilities of the complexes of ligands, such as isophthalate, 4-methoxybenzoate, 2,4-dimethoxybenzoates, and benzylidenepyruvates are enhanced by intraligand charge polarization [1,4]. An absence of the polarizing effect for the mono-methoxybenzoate complexes was also reported [6]. We have shown that the theoretical calculation of the charge distributions on the carbon atoms of the ligands would be useful to prove the presence of resonance and inductive effects of the ligand in the complexation [1].

As an extension of our studies regarding the effect of substituents of the aromatic monocarboxylate

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ligands on the lanthanide complexation, thermodynamic studies of the complexation of lanthanides with some benzoic acid derivatives have been carried out. The following benzoic acid derivatives are studied: 4-nitrobenzoate; 4-hydoxybenzoate; and 4-aminobenzoate. The charge distributions on the carbon atoms of various aromatic ligands have also been calculated in the ionized form and the metal complexed form, respectively. In the calculations of the metal complexes, Al(III), instead of La(III), was used as a model ion to avoid the complexity in the calculation.

2. Experimental

2.1. Chemicals

Stock solutions of the lanthanide perchlorates were prepared by dissolving lanthanide oxides, La_2O_3, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, and Lu_2O_3 (Aldrich, 99.99%) in hot concentrated perchloric acid (Aldrich, 69.0–72.0%). The concentrations of the stock solutions were standardized by EDTA titration with xylenol orange indicator in acetate buffer solution. The standard EDTA solution was standardized by titration with ammonia buffer solution of pure refined Zn metal using Eriochrome Brack T as an indicator. Stock solutions of the metal ions were kept below pH 3.5 in order to prevent precipitation due to hydrolysis at higher pH. The working solutions were prepared from the stock solutions by adjusting to suitable pH after diluting to appropriate concentrations.

The ligand acids (4-aminobenzoic acid, 4-hydroxybenzoic acid, and 4-nitrobenzoic acid) were obtained in the reagent grade form from Aldrich and used without further purification. The stock solutions of the ligand acids were prepared by dissolving appropriate weights in standard sodium hydroxide solution and their concentrations were standardized by acid–base titration. Deionized water was used for the preparation of all the solutions. The ionic strength of the solutions was adjusted to 0.10 M with sodium perchlorate.

2.2. Apparatus

The potentiometric measurements were performed using a Metrom model 654 digital pH-meter in conjunction with a Metrom combination electrode. The KCI solution of the electrode was replaced with 4.0 M LiCl solution to prevent precipitation of $KClO_4$. The pH meter was calibrated before the titration using standard buffer solutions (Merck) of pH 7.00 and 4.00, respectively. The titrations were conducted at $25.0 \pm 0.1^\circ C$ using a jacketed vessel connected to a circulating water bath. The calorimetric titrations were performed on a Tronac Model 458 titration calorimeter.

2.3. Procedures

Potentiometric titrations were used to determine the dissociation constants of the ligand acids and the stability constants of the lanthanide complexes with the similar procedure described previously [4]. The dissociation constants were determined by titration of the ligand acid solutions($\sim 4.0 \times 10^{-3}$ M) with standard NaOH solution ($\sim 1.0 \times 10^{-1}$ M). The stability constants of the complexes were evaluated by titrations of the mixtures of lanthanide perchlorates and sodium salts of the ligand anions with standardized NaOH solution. The determined values were obtained by minimization of the error-squares sums, U, defined as:

$$U = \sum w_i (\mathrm{pH}_{\mathrm{obs}} - \mathrm{pH}_{\mathrm{calc}})^2 \quad (1)$$

where w_i is the weighing factor assigned to each point of the titration curve and $\mathrm{pH}_{\mathrm{obs}}$ and $\mathrm{pH}_{\mathrm{calc}}$ refer to the observed and calculated pH values, respectively. The latter one was obtained on the basis of the assumed model, consisting of a set of (p,q,r) complexes. The corresponding stability constants were estimated according to Eq. (3):

$$pM^{3+} + qH^+ + rL^{3-} \rightleftharpoons M_pH_qL_r \quad (2)$$

$$\beta_{pqr} = [M_pH_qL_r]/[M^{3+}]^p[H^+]^q[L^-]^r \quad (3)$$

The minimization in Eq. (1) was performed with the aid of the program BEST [7].

Calorimetric titrations were used to determine the enthalpies of protonation of the ligands and the enthalpies of complexation of the lanthanide complexes. The general procedure for the calorimetric titration has been described in the literature [8]. The heats of protonation of the ligand acids were obtained by titrating calorimetrically the ligand salt solutions of the ligands with a standard HCI solution. The heats of formation of the lanthanide complexes were determined by subtracting the heats of dilution and protonation of the ligand from the heat obtained by titration of the lanthanide perchlorate solutions with the ligand buffer solution. The heats of dilution of the ligand were determined by titration of the ligand solution into 0.10 M NaClO$_4$ solution. The total ionic strength of the working solutions was adjusted to 0.10 M NaClO$_4$. The titration data were treated by linear least-squares analysis to obtain the enthalpies of complexation ΔH_{101} according to the Eq. (4):

$$Q_{\mathrm{LnL}} = (\Delta n_{\mathrm{LnL}})\Delta H_{101} \qquad (4)$$

where Q_{LnL} and Δn_{LnL} are the changes as a results of the complexation and the change of the moles of LnL^{2+} formed in the titration, respectively.

The theoretical calculations were performed with HyperChem Release 3 computational program (Autodesk, 1993). All calculations were carried out with complete geometry optimization.

3. Results and discussion

3.1. Thermodynamics

The acid dissociation constants of the ligand acids and the stability constants of their complexes with the lanthanide cations were determined by potentiometric titration. The pK_a, values obtained for 4-aminobenzoic, 4-hydroxybenzoic, and 4-nitrobenzoic acids were 4.81, 4.06, and 3.35, respectively, in the ionic medium of 0.1 M NaCIO$_4$ at 25°C. The stability constants of the lanthanide complexes of 4-aminobenzoate, 4-hydroxybenzoate, and 4-nitrobenzoate are given in Table 1.

Fig. 1 represents the relationship between the stability constants (log β_{101}) and the basicities (pK_a) of the ligands for a number of Sm(III) complexes with aliphatic and aromatic monocarboxylate ligands in aqueous solution. The data are collected from the literature [3,4,6,9,10]. The values have been adjusted to an ionic strength of 0.10 M in NaCIO$_4$ solution [3]. As was expected, two groups of the linear correlations of log β_{101} and pK_a occur, one for the aliphatic, and the other for the aromatic monocarboxylates. The linear

Table 1
Stability constants (log β_{101}) of the Ln(III) complexes with 4-aminobeozoate, 4-hydroxybeozoate, and 4-nitrobenzoate: $\mu = 0.1$ M (NaCIO$_4$); and $T = 298$ K

Ion	4-Aminobenzoate	4-Hydroxybenzoate	4-Nitrobenzoate
La	1.93 ± 0.01	1.71 ± 0.01	1.59 ± 0.02
Nd	2.17 ± 0.01	1.83 ± 0.01	1.81 ± 0.02
Sm	2.26 ± 0.02	1.93 ± 0.01	1.89 ± 0.01
Eu	2.12 ± 0.01	1.89 ± 0.01	1.78 ± 0.02
Gd	2.10 ± 0.01	1.85 ± 0.02	1.73 ± 0.01
Dy	1.98 ± 0.01	1.64 ± 0.01	1.63 ± 0.01
Ho	1.94 ± 0.02	1.72 ± 0.01	1.62 ± 0.01
Er	1.94 ± 0.01	1.70 ± 0.01	1.67 ± 0.01
Yb	1.96 ± 0.01	1.69 ± 0.04	1.68 ± 0.02
Lu	1.96 ± 0.01	1.61 ± 0.01	1.67 ± 0.01

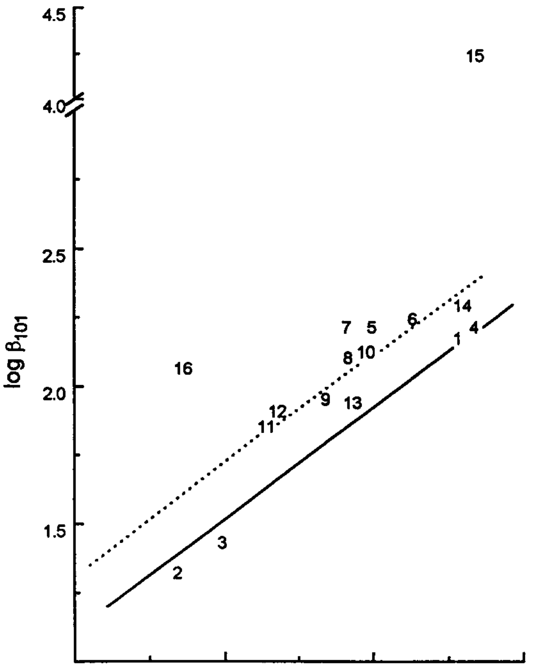


Fig. 1. Relationship between the stability constants (log β_{101}) and the basicities (pK_a) of the ligands for Sm(III)-L complexes, where L is: 1, acetate [11]; 2, chloroacetate [11]; 3, iodoacetate [11]; 4, propionate [11]; 5, benzoate [3]; 6, 4-methoxybenzoate [6]; 7, 3-methoxybenzoate [6]; 8, 2-methoxybenzoate [6]; 9, 3-fluorobenzoate [4]; 10, 4-fluorobenzoate [4]; 11, 3-nitrobenzoate [4]; 12, 4-nitrobenzoate; 13, 4-hydroxybenzoate; 14, 4-aminobenzoate; 15, anthranilate [9]; and 16, salicylate [10].

curve for the aromatic carboxylate lies a little higher than that for the aliphatic carboxylate, reflecting the enhancement of the stability by the resonance effect of the phenyl ring. If the charge polarization by lanthanide cations is likely to occur, the values of stability constant of 4-nitrobenzoate and 4-hydroxybenzoate are assumed to be above the linear curve, since $–NO_2$ and –OH are such strong electron-withdrawing groups. However, the correlation does not precisely show the effects of the substituents of the phenyl ring. The salicylate and anthranilate in Fig. 1 are located well above the line, indicating that *ortho*-hydroxy and *ortho*-amino groups of phenyl ring would be involved in the chelate formation of the cation with the carboxylate group of the ligands [9,10,12].

The thermodynamic parameters for 4-aminobenzoate, 4-hydroxybeazoate, and 4-nitrobenzoate complexes of lanthanide cations have been measured by calorimetric titration. Enthalpies of protonation of 4-aminobenzoic acid, 4-hydroxybenzoic acid, and 4-nitrobenzoic acid were determined as -0.26, -2.14 and $-0.27\ \mathrm{kJ\ mol^{-1}}$, respectively. Table 2 summarizes the thermodynamic parameters calculated for the formation of 4-aminobenzoate, 4-hydroxy-

Table 2
Thermodynamic parameters for complexation of lanthanides by 4-aminobenzoate, 4-hydroxybenzoate, and 4-nitrobenzoate: $\mu = 0.1$ M $NaClO_4$; and $T = 298$ K

Ion	$-\Delta G_{101}$/ (kJ $\mathrm{mol^{-1}}$)	ΔH_{101}/ (kJ $\mathrm{mol^{-1}}$)	ΔS_{101}/ (J $\mathrm{K^{-1}\ mol^{-1}}$)
(a) *Lanthanide-4-aminobenzoate*			
La	11.03 ± 0.04	5.80 ± 0.09	56.5 ± 0.2
Nd	12.39 ± 0.04	7.18 ± 0.10	65.6 ± 0.4
Sm	12.90 ± 0.05	7.53 ± 0.05	68.5 ± 0.3
Eu	12.10 ± 0.06	7.50 ± 0.05	65.7 ± 0.2
Gd	11.99 ± 0.05	7.91 ± 0.12	66.7 ± 0.3
Dy	11.30 ± 0.07	11.59 ± 0.36	76.8 ± 0.4
Ho	11.07 ± 0.02	12.58 ± 0.02	79.3 ± 0.2
Er	11.07 ± 0.04	11.21 ± 0.15	74.7 ± 0.2
Yb	11.19 ± 0.08	13.20 ± 0.10	81.8 ± 0.3
Lu	11.19 ± 0.07	12.60 ± 0.11	79.8 ± 1.0
(b) *Lanthanide-4-hydroxybenzoate*			
La	9.76 ± 0.10	8.64 ± 0.10	61.7 ± 0.3
Nd	10.05 ± 0.04	8.52 ± 0.05	63.6 ± 0.3
Sm	10.07 ± 0.02	7.82 ± 0.02	60.0 ± 0.4
Eu	10.79 ± 0.05	9.06 ± 0.02	66.6 ± 0.4
Gd	10.56 ± 0.05	10.14 ± 0.09	69.4 ± 0.2
Dy	9.36 ± 0.06	12.44 ± 0.06	73.1 ± 0.4
Ho	9.82 ± 0.04	11.41 ± 0.02	71.2 ± 0.4
Er	9.70 ± 0.02	13.84 ± 0.05	79.0 ± 0.1
Yb	9.65 ± 0.05	13.09 ± 0.02	76.3 ± 0.4
Lu	9.19 ± 0.03	12.03 ± 0.02	71.2 ± 0.3
(c) *Lanthanide-4-nitrobenzoate*			
La	9.08 ± 0.10	7.10 ± 0.85	54.2 ± 0.7
Nd	10.33 ± 0.05	6.10 ± 0.55	55.1 ± 0.4
Sm	10.79 ± 0.03	5.90 ± 0.50	56.0 ± 0.3
Eu	10.16 ± 0.10	7.05 ± 0.43	57.6 ± 0.3
Gd	9.87 ± 0.05	7.60 ± 0.49	58.6 ± 0.9
Dy	9.30 ± 0.06	8.69 ± 0.71	60.4 ± 1.2
Ho	9.25 ± 0.05	8.10 ± 0.52	58.2 ± 0.3
Er	9.53 ± 0.05	10.07 ± 0.35	65.8 ± 0.2
Yb	9.59 ± 0.02	9.24 ± 0.10	63.2 ± 0.7
Lu	9.53 ± 0.05	8.87 ± 0.05	61.7 ± 0.2

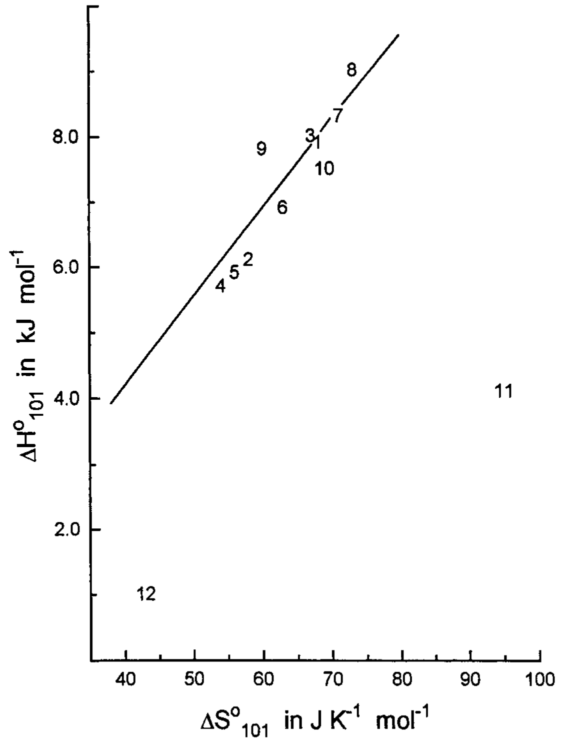


Fig. 2. Correlation of the enthalpy of complexation ΔH_{101} and the entropy of complexation ΔS_{101} for Sm(III)-L complexes, where L is: 1, benzoate [3]; 2, 3-fluorobenzoate [4]; 3, 4-fluorobenzoate [4]; 4, 3-nitrobenzoate [4]; 5, 4-nitrobenzoate; 6, 2-methoxybenzoate [6]; 7, 3-methoxybenzoate [6]; 8, 4- methoxybenzoate[6]; 9, 4-hydroxybenzoate; 10, 4-aminobenzoate; 11, anthranilate[9]; and 12, salicylate [12].

benzoate, and 4-nitrobenzoate complexes of lanthanide cations.

Fig. 2 is a plot of the correlation of the enthalpy of complexation ΔH_{101} and the entropy of complexation ΔS_{101} for Sm(III) complexes of various benzoic acid derivatives [3,4,6,9,12]. Fig. 2 shows that lanthanide complexes of benzoic acid derivatives is over line related to isothermodynamics. From the slope of the linear relationship it can be deduced that the isothermodynamic temperature is 162 K. Accordingly, because this is lower than the experimental temperature (298 K), the complex formation reaction is derived from the increase in entropy according to the destruction of hydration structure of cations and anions.

The salicylate and anthranilate on Fig. 2 deviate from isothermodynamic relationship, indicating that *ortho*-hydroxy and *ortho*-amino groups of phenyl ring would be involved in the chelate formation of the cation with the carboxylate group [9–11].

3.2. Theoretical calculation

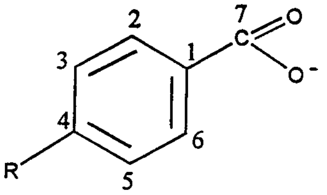
Theoretical calculations of the charge distributions of various carboxylate anions and their metal complexes have been made. In the theoretical calculations of the metal complexes, Al^{3+} ion was used as a model ion for Ln^{3+} ions. As representative data, Table 3 summarizes the calculated charge distributions on the carbon atoms of ligand for 4-aminobenzoate, 4-nitrobenzoate, and 4-hydroxybenzoate. The charge shift (Δq) is defined as the difference between the charges (q_L and q_{ML}) on the carbon atoms of the ligand

Table 3
The calculated charge distribution on the carbon atoms of ligands for 4-aminobenzoate, 4-nitrobenzoate, and 4-hydroxybenzoate.

Number of C atoms	Charge		
	q_L [a]	q_{ML} [b]	$\Delta q(q_{ML}-q_L)$
(a) *4-Aminobenzoate*			
1	−0.150	−0.118	+0.032
2	−0.066	+0.019	+0.085
3	−0.239	−0.208	+0.031
4	+0.083	+0.252	+0.169
5	−0.239	−0208	+0.031
6	−0.066	+0.019	+0.085
7	+0.360	+0.306	−0.054
(b) *4-Nitrobenzoate*			
1	−0.057	−0.143	−0.086
2	−0.125	+0.010	+0.135
3	−0.094	−0.112	−0.018
4	−0.162	+0.044	+0.206
5	−0.094	−0.112	−0.018
6	−0.125	+0.010	+0.135
7	+0.355	+0.455	+0.100
(c) *4-Hydroxybenzoate*			
1	−0.132	−0.146	−0.014
2	−0.080	+0.028	+0.108
3	−0.185	−0.179	+0.006
4	+0.038	+0.300	+0.262
5	−0.239	−0.246	−0.007
6	−0.075	+0.051	+0.126
7	+0.359	+0.362	+0.003

[a] The charges on the carbon atoms of the ligand ion.
[b] The charges on the carbon atoms of the AI(III) complex ion.

ion and metal complex ion. Numbering of the carbon atoms of the ligand is given below.



It is interesting to note that positive shifts ($\Delta q > 0$) of charges of all carbon atoms, beside the number seven atom of the ligand, occur only for the 4-aminobenzoate from ionized form to the metal complexed form. Since the amine group of the phenyl ring is a strong electron-donating group, it is quite reasonable that the negative shift of charge ($\Delta q < 0$) of the carboxylate carbon (number seven carbon) occurs through electron flowing from the amine group to the carboxylate carbon by the resonance and inductive charge polarization caused by the trivalent metal cation. On the other hand, for the 4-nitrobenzoate and 4.-hydroxybenzoate which have electron-withdrawing substituents, the positive shift ($\Delta q > 0$) of the charge of the carboxylate carbon occurs. As would be expected, the higher stability of the complex results because of the more negative charge shift of the carboxylate carbon of the ligand.

In order to generalize the relationship between the stability constant and the charge shift (Δq) of the metal complex, the charge of the carboxylate carbon (number seven carbon) of various substituted benzoate complexes has been calculated. Table 4 gives calculated charge shifts (Δq) of carboxylate carbon atoms of the ligands along with the stability constants ($\log \beta_{101}$) of the samarium complexes. Fig. 3 shows the plot of the data given in Table 4. It gives a roughly linear relationship between the stability constant and the charge shift, demonstrating that the stability constants of the complexes increase with the increase in the negative charge shifts of carboxylate carbon atoms of substituted benzoate ligands while changing from the ionized form to the metal complexed form.

Table 4
Charge shift (Δq) of the carboxylate carbon (number seven) of the ligands and stability constants for various Sm(III)-carboxylate complexes: $\mu = 0.1$ M $NaClO_4$; and $T = 298$ K

Ligands	Δq	$\log \beta_{101}$	Ref.
Benzoate	+0.067	2.21	[3]
3-Methoxybenzoate	+0.072	2.21	[6]
4-Methoxybenzoate	−0.014	2.24	[6]
3-Fluorobenzoate	+0.079	1.95	[4]
4-Fluorobenzoate	+0.043	2.12	[4]
3-Nitrobenzoate	+0.086	1.85	[4]
4-Nitrobenzoate	+0.100	1.89	This work
4-Aminobenzoate	−0.054	2.26	This work
4-Hydroxybenzoate	+0.003	1.93	This work
Iso-phthalate	−0.166	2.82	[3]

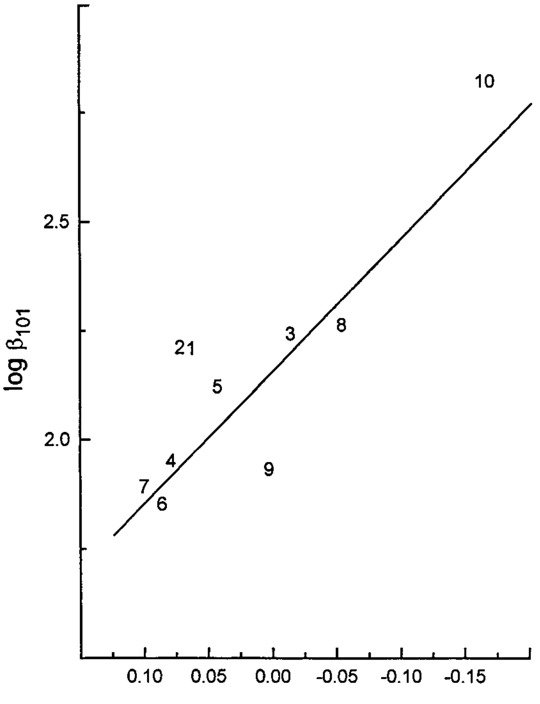


Fig. 3. Relationship between stability constants ($\log \beta_{101}$) of Sm(III)-L complexes and calculated charge shifts (Δq) of carboxylate carbon atoms of the ligands L, where L is: 1, benzoate; 2, 3-methoxybenzoate; 3, 4-methoxybenzoate; 4, 3-fluorobeazoate; 5, 4- fluorobenzoate; 6, 3-nitrobenzoate; 7, 4-nitrobenzoate; 8, 4-aminobenzoate; 9, 4-hydroxybeazoate; and 10, iso-phthalate.

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