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Thermodynamics of complexation of lanthanides by various dimethoxybenzoates in aqueous solution

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Abstract

The stability constants of the complexes of trivalent lanthanide cations with various dimethoxybenzoates have been determined by the potentiometric titration method. The dimethoxybenzoates studied were 2,3-dimethoxybenzoate, 2,4-dimethoxybenzoate, and 2,5-dimethoxybenzoate. The thermodynamic parameters for the complexation of some lanthanide cations with 2,5-dimethoxybenzoate were measured by enthalpy titration using a titration calorimeter. All complexation measurements were made at 25°C in an aqueous medium of ionic strength 0.5 M $NaClO_4$. The thermodynamic parameters for the complexation are discussed in relation to the electronic effect of the substituent groups within the ligand. It is proposed that the enhanced stability of the dimethoxybenzoate complexes of lanthanide cations is mainly due to the polarization of the electronic charge density from the methoxy groups through the π-system of the phenyl ring to the caboxylate group. ^{13}C NMR evidence for charge polarization by the lanthanide cation in the complexation is presented. Theoretical calculations of the charge distributions on the carbon atoms of the 2,4-dimethoxybenzoates were also performed.

Keywords: Charge density; Complexation; Dimethoxybenzoate; Lanthanon; Stability; Thermodynamics

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1. Introduction

Thermodynamic studies on the complexation of trivalent lanthanide cations with various carboxylic acid derivatives are extensive [1-15]. Choppin and coworkers studied the complexation of trivalent lanthanide cations with various aryl monocarboxylic acids such as benzoic acid [10], 3-fluorobenzoic acid, 4-fluorobenzoic acid, and 3-nitrobenzoic acid [11]. It has been found that the stability constants of the aryl monocarboxylates show a linear correlation with the acidity constants of the ligands, like those of alkyl monocarboxylates [11,12]. The positive values of both the enthalpy and entropy of complexation and the compensation between them have been attributed to the dehydration of the metal and ligand ions in the overall complexation. However, the stability constants of the isophthalate complexes of lanthanide cations are larger than would be expected from a linear correlation of the stability constants with the acidity constants of the ligands [11]. This enhanced stability of the isophthalate complexes could be interpreted with reference to intraligand charge polarization [11,12]. The intraligand charge polarization effect has also been observed in the complexation of lanthanide cations with benzylidenepyruvates [13,15] and methoxybenzoates [11]. However, evidence for an absence of the polarizing effect was later reported for the methoxybenzoate complexation systems [14].

In this paper, we report thermodynamic studies of the complexation of lanthanides with some isomers of dimethoxybenzoic acids. These ligands have the potential to increase the basicity of the carboxylate group in the complexation via the cation-induced transmission of electronic charge density from the methoxy groups.

2. Experimental

2.1. Chemicals

Stock solutions of the lanthanide perchlorates were prepared by dissolving the lanthanide oxides (Aldrich Co. 99.99%) in hot concentrated perchloric acid and diluting them with deionized water to the appropriate concentrations. The concentrations of the stock solutions were standardized by EDTA titration with xylenol orange indicator in acetate buffer. Stock solutions of the metal ions were kept below pH 4 to prevent precipitation by hydrolysis of the metal ion. The ligand acids, 2,3-dimethoxybenzoic acid, 2,4-dimethoxybenzoic acid, and 2,5-dimethoxybenzoic acid, were obtained in 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 solutions. The ionic strength of the solutions was adjusted to 0.50 M with sodium perchlorate.

2.2. Apparatus

The potentiometric (pH) titrations were performed using a Beckman 4500 digital pH-meter in conjunction with a Fisher standard combination electrode. The KCl 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 (Anachemica Tedia Co.) of pH 7.00 and 4.00. The titrations were conducted at 25.0 ± 0.1°C using a jacketed vessel connected to a circulating water bath. The calorimetric titrations were performed on a titration calorimeter which is similar to the commercially available Tronac Model 450 calorimeter. Carbon-13 magnetic resonance spectra were obtained with a 300 MHz NMR spectrometer (Bruker AM-300) using the pulsed Fourier transform mode with a deuterium lock.

2.3. Procedures

The general reaction studied was

$$Ln^{3+} + L^- \rightleftharpoons LnL^{2+} \tag{1}$$

with a stability constant defined by

$$\beta_{101} = [LnL^{2+}]/[Ln^{3+}][L^-] \tag{2}$$

where [ ] represents concentration in 0.5 M ($NaClO_4$) ionic medium. Potentiometric titrations were used to determine the acid constants of the ligands and the stability constants of the lanthanide complexes. The procedure for the potentiometric titration has been described previously [8]. The proton dissociation constants of the ligands were determined by titrating a 20.0 ml aliquot of the ligand acid solution with standard NaOH solution. The stability constants of the lanthanide complexes were determined by titrations of lanthanide perchlorate solutions with the buffer solution of the ligands. The measured pH values were converted to hydrogen ion concentrations from a calibration curve of the glass electrode which was obtained using solutions of known hydrogen ion concentrations. From the pH data, the average number of ligands bound per cation $\bar{n}$ was calculated. A linear least-squares analysis of Eq. (3) gave the values of β_{101} [16]. In all titrations, the ratio of the concentrations of the cation and the ligand was maintained such that ML_2 complexes were not formed

$$\frac{\bar{n}}{1-\bar{n}} = \beta_{101}[L] \tag{3}$$

where [L] is free ligand concentration.

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 [17]. The heats of protonation of the ligand acid were obtained by titrating calorimetrically the ligand salt solutions of the ligands with a standard HCl 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 0.50 M $NaClO_4$ solution. The total ionic strength of the working solutions was adjusted to 0.50 M with $NaClO_4$. The titration data were treated by linear least-squares analysis to obtain the enthalpies of complexation ΔH_{101} according to the Eq. (4)

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

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

^{13}C NMR measurements were obtained at ambient temperature with DSS (sodium 2,2-dimethyl-2-silapentane-5-sulphonate) as internal standard. The concentrations of all working solutions for NMR study were 0.01 M, with a pH value above 6.00.

The theoretical calculations were performed with the semi-empirical AM1 method [18]. All calculations were carried out with complete geometry optimization.

3. Results and discussion

3.1. Thermodynamics

The acid dissociation constants of 2,3-, 2,4-, and 2,5-dimethoxybenzoic acid and the stability constants of their complexes with the lanthanide cations were determined by potentiometric titration. The pK_a values obtained for 2,3-, 2,4-, and 2,5-dimethoxybenzoic acid were 3.19, 4.32, and 3.61, respectively, in the ionic medium of 0.5 M $NaClO_4$ at 25°C. The stability constants of the lanthanide complexes of the three isomers of dimethoxybenzoate are given in Table 1.

Table 1
Stability constants ($\log \beta_{101}$) of the Ln(III)-dimethoxybenzoate complexes: $\mu = 0.5$ M ($NaClO_4$); $T = 298$ K

Ion	2,3-DMBH	2,4-DMBH	2,5-DMBH
La	2.59 ± 0.01	2.88 ± 0.01	2.87 ± 0.01
Nd	2.52 ± 0.01	2.88 ± 0.01	2.77 ± 0.01
Sm	2.54 ± 0.01	2.91 ± 0.01	2.84 ± 0.01
Eu	2.58 ± 0.01	2.83 ± 0.01	2.67 ± 0.01
Gd	2.42 ± 0.01	2.85 ± 0.01	2.68 ± 0.01
Dy	2.45 ± 0.01	2.78 ± 0.01	2.68 ± 0.01
Ho	2.46 ± 0.01	2.75 ± 0.01	2.64 ± 0.01
Er	2.48 ± 0.01	2.71 ± 0.01	2.72 ± 0.01
Yb	2.48 ± 0.01	2.84 ± 0.01	2.68 ± 0.01
Lu	2.50 ± 0.01	2.83 ± 0.01	2.72 ± 0.01

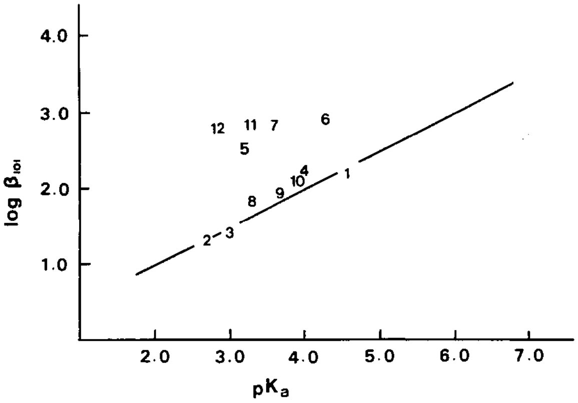


Fig. 1. Relationship between log β_{101} and pK_a of SmL^{2+} complexes where L is: 1, acetate [19]; 2, chloroacetate [19]; 3, iodoacetate [19]; 4, benzoate [10]; 5, 2,3-dimethoxybenzoate; 6, 2,4-dimethoxybenzoate; 7, 2,5-dimethoxybenzoate; 8, 3-nitrobenzoate [11]; 9, 3-fluorobenzoate [11]; 10, 4-fluorobenzoate [11]; 11, isophthalate [10]; 12, fumarate [7].

Fig. 1 represents the relationship between the stability constants (log β_{101}) and the basicities (pK_a) of the ligands for the monocarboxylate complexes of samarium(III) ion in aqueous solution. Fumarate [7] and iso-phthalate [10] are dicarboxylates, but only one carboxylate group of the ligands coordinates to the metal ion. Fig. 1 is based on the data collected from the literature [7,10,11,19]. All values were obtained in a 0.1 M ionic medium, except those for the isomers of dimethoxybenzoate (0.5 M $NaClO_4$). However, direct comparison is possible, keeping in mind that the stability constant of the complex generally increases with decreasing ionic strength of the solution. The stability constants (log K_1) of aliphatic carboxylate complexes with trivalent lanthanide cations increase by about 0.3 with decreasing ionic strength of the system from 0.5 M to 0.1 M [20]. The stability constants of the complexes of 2,3-, 2,4-, and 2,5-dimethoxybenzoate fall above the correlation line, together with those of fumarate and iso-phthalate. This extra stability of the fumarate [7] and iso-phthalate [10] has been interpreted in terms of an intraligand charge polarization due to the lanthanide cations. The inductive charge polarization could also be applied to explain the enhanced stability of complexes of the isomers of dimethoxybenzoate. The electronic charge on the methoxy group at the para-, ortho-, or meta-position of the ligand flows to the carboxylate group to which the multiply charged lanthanide cation is bound. Thus, the negative charge on the carboxylate group would be increased by the cation in the complex. The intraligand charge polarization in the dimethoxybenzoates would contribute to the stronger binding between the carboxylate group of the ligand and the lanthanide cation.

The thermodynamic parameters for 2,5-dimethoxybenzoate complexes of lanthanide cations have been measured by calorimetric titration which was unable to measure those for the 2,3- and 2,4-dimethoxybenzoate systems because of their low solubility in water. The enthalpy of protonation of 2,5-DMBH was determined as 3.33 kJ mol^{-1}. Table 2 summarizes the thermodynamic parameters calculated for the formation of 2,5-dimethoxybenzoate complexes of lanthanide cations.

Table 2
Thermodynamic parameters for Ln(III)-2,5-dimethoxybenzoate complexation: $\mu = 0.5$ M $NaClO_4$; $T = 298$ K

Ion	$-\Delta G_{101}$ in kJ mol^{-1}	ΔH_{101} in kJ mol^{-1}	ΔS_{101} in J K^{-1} mol^{-1}
Nd	5.8 ± 0.1	3.5 ± 1.2	65 ± 5
Sm	16.2 ± 0.1	5.4 ± 0.2	72 ± 1
Eu	15.3 ± 0.1	2.8 ± 0.4	61 ± 2
Dy	15.3 ± 0.1	4.6 ± 0.6	67 ± 2
Ho	15.1 ± 0.1	5.2 ± 0.2	68 ± 1
Er	15.5 ± 0.1	5.2 ± 0.4	69 ± 2
Yb	15.3 ± 0.1	6.6 ± 0.6	73 ± 2
Lu	15.5 ± 0.1	5.6 ± 0.6	71 ± 3

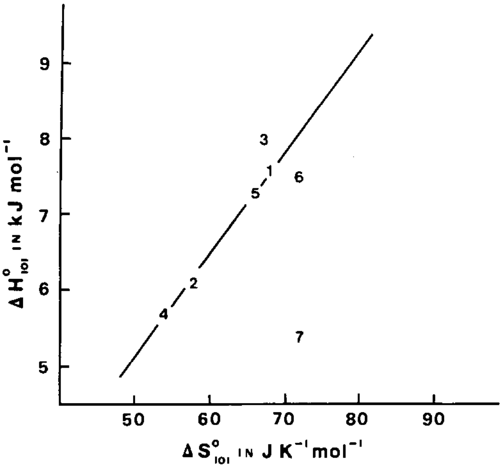
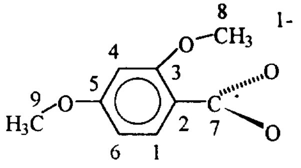


Fig. 2. Relationship between ΔH_{101} and ΔS_{101} of SmL^{2+} complexes where L is: 1, benzoate [10]; 2, 3-fluorobenzoate [11]; 3, 4-fluorobenzoate [11]; 4, 3-nitrobenzoate [11]; 5, 3-hydroxybenzoate [14]; 6, 4-hydroxybenzoate [14]; 7, 2,5-dimethoxybenzoate.

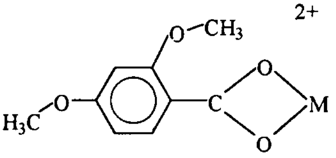
Fig. 2 is a plot of the correlation of the enthalpy of complexation ΔH_{101} and the entropy of complexation ΔS_{101} for Sm(III) complexes of benzoic acid derivatives [10,11,14] including the 2,5-dimethoxybenzoate. Fig. 2 shows that the enthalpy of complexation of the 2,5-dimethoxybenzoate is approx. 2.6 kJ mol^{-1} less endothermic without a compensating change in the entropy of complexation, which implies stronger binding between the carboxylate anion and the samarium cation as compared to the other benzoates. This is further evidence for the existence of intraligand charge polarization in dimethoxybenzoate ligands. This approx. 2.6 kJ mol^{-1} greater exothermicity would be compensated with approx. 19 J mol^{-1} K^{-1} less positive entropy change, if there is an absence of intraligand charge polarization in the complexation.

3.2. Carbon-13 NMR and theoretical calculation

^{13}C NMR spectra of sodium salts of benzoate and 2,4,-dimethoxybenzoate, and of lanthanum complexes of benzoate (1:1) and lanthanum 2,4-methoxybenzoate (1:1), have been measured in aqueous solution. Theoretical calculations of the charge distributions of these species have also been performed. In the theoretical calculations of the metal complexes, we used Al^{3+} as a model ion instead of La^{3+}. It is observed that the chemical shift of the carboxylate carbon of the benzoate shifts 1.03 ppm downfield from 178.25 ppm for the sodium salt to 179.35 ppm for the lanthanum complex. This observation agrees well with the calculated charge of the carboxylate carbon of the benzoate. The positive charge of the carboxylate carbon of the benzoate is increased by 0.0663 from $+0.3551$ in the benzoate anion to $+0.4214$ in the benzoate complex with trivalent metal cation. In the system of 2,4-dimethoxybenzoate, the chemical shift of the carboxylate carbon moves 6.18 ppm upfield from 178.19 ppm for the sodium salt to 172.01 ppm for the lanthanum complex. This observation is further evidence for the existence of an intraligand charge polarization in the lanthanide complexation of 2,4-dimethoxybenzoate. There are two possible conformations of 2,4-dimethoxybenzoate, as shown below with numbering of the carbon atoms; one is the conformation (**I**) in which the carboxylate group is perpendicular to the molecular plane, and the other (**II**) is one in which the carboxylate, the phenyl, and the *o*- and *p*-methoxy groups are coplanar, see Formulae 1 and 2.



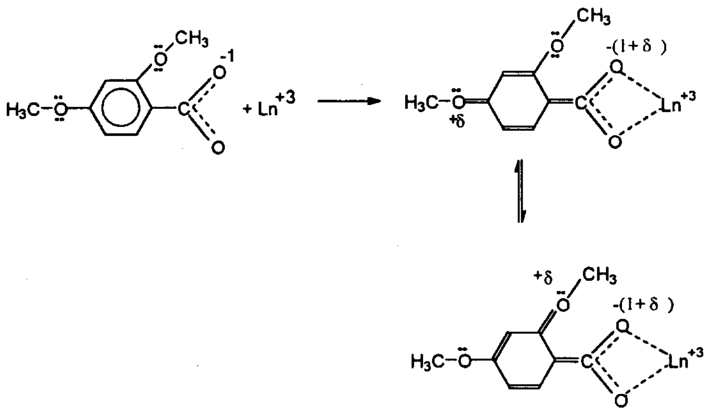
Formula 1. Compound **I**.



Formula 2. Compound **II**.

Theoretical calculations of the enthalpies of formation show that (**I**) is preferable to (**II**) by 11.42 kJ mol^{-1} in the ionized form, while (**II**) is preferable to (**I**) by 75.34 kJ mol^{-1} in the form complexed with trivalent metal cation. The coplanarity is apparently prohibited by the steric hindrance of the ortho-methoxy group in the ionized form. However, in the complexed form with trivalent metal cation, the effect of resonance and inductive charge polarization caused by the metal ion would overcome the steric effect and favour the coplanarity of the ligand. This strongly suggests the presence of both resonance and inductive polarization in the 2,4-dimethoxybenzoate complex. The resonance and inductive effect would be written as shown in Formula 3.

The calculated charge distributions on the carbon atoms of the ligand also support the presence of resonance and inductive effects. Table 3 summarizes the calculated charge distributions on the carbon atoms of 2,4-dimethoxybenzoates. As



Formula 3. The resonance and inductive effect.

Table 3
The calculated charge distribution on the carbon atoms of 2,4-dimethylbenzoate species

Number of C atoms	Charge		
	q_L	q_{ML}	Δq
1	−0.0630	+0.0123	+0.0753
2	−0.1620	−0.1329	+0.0291
3	+0.1218	+0.2606	+0.1388
4	−0.2059	−0.3117	−0.1058
5	+0.0621	+0.3003	+0.2382
6	−0.2479	−0.2181	+0.0298
7	+0.3610	+0.3474	−0.0136
8	−0.0922	−0.0867	+0.0055
9	−0.0662	−0.0947	−0.0285

Key: q_L and q_{ML} are the charges on the carbon atoms of the ligand ion and metal complex ion, respectively.

expected, the charge of the carboxylate carbon (number seven carbon), together with that of the number four carbon, in the ionized form becomes more negative in the metal complexed form. This is parallel with the upfield chemical shift of the carboxylate carbon from 178.19 ppm of the sodium salt to 172.01 ppm of the lanthanum complex in the ^{13}C NMR study of 2,4-dimethoxybenzoate.

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