

Complexation Thermodynamics of Lanthanoids(III) with 3-Bromo-5-sulfosalicylic Acid

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Complex formation equilibria in the lanthanoid(III)–3-bromo-5-sulfosalicylate (H_2L^-) system has been studied by potentiometric titration over the pH range 2–9. The measurements were performed in 0.10 M $NaClO_4$ at 25°C. The data indicate the formation of the species $[Ln(HL)]^+$, $[LnL]$, $[LnL_2]^{3-}$, $[Ln(OH)L]^-$ and $[Ln(OH)_2L]^{2-}$. Enthalpy values were obtained for the $[Ln(HL)]^+$ complexes by calorimetric titrations. The mode of complexation was studied by ^{13}C NMR spectroscopy. The results are compared with data for complexation by various aromatic hydroxycarboxylic acids.

The stability of lanthanoid(III) complexes with alkyl and aryl monocarboxylate anions has correlated well with the anionic basicity as measured by the pK_a values of the parent acids.^{1–3} The stability constants of lanthanoid(III) complexes with many sulfo-substituted aromatic *o*-hydroxycarboxylic acids also show a linear correlation with pK_a , but these are more than an order of magnitude greater than those for the lanthanoid(III) monocarboxylates.⁴ We have recently studied the thermodynamic parameters for formation of the lanthanoid(III) complexes with 2,4-, 2,5- and 3,5-dihydroxybenzoic acids.⁵ The stability for the 3,5-dihydroxycarboxylato complex falls on the common line of alkyl and aryl monocarboxylato complexes, but the values for 2,4- and 2,5-dihydroxycarboxylates lie between this line and the line of various aromatic sulfo-substituted *o*-hydroxycarboxylato ligands.

The thermodynamic data obtained in the present study for the lanthanoid(III)–3-bromo-5-sulfosalicylic acid system are contrasted with those for the lanthanoids(III) complexing with the sulfo-substituted and unsubstituted aromatic hydroxycarboxylic acid ligands in order to clarify the factors involved in the formation of the complexes of lanthanoids(III) with aromatic hydroxycarboxylic acids.

Experimental

Reagents. Stock solutions of lanthanoid(III) perchlorates were prepared and analyzed as described elsewhere.¹

3-Bromo-5-sulfosalicylic acid was prepared by bromating 5-sulfosalicylic acid at 25–45°C. The white product was recrystallized three times from hot water. The purity

of the compound was determined by 1H NMR spectroscopy and by titration with standardized NaOH solution.

Perchloric acid (Merck, p.a.) was standardized by titration with TRIS (hydroxymethylaminomethane) using bromocresol green–methyl red (3:2) as an indicator.

NaOH stock solution was standardized by titration with potassium hydrogen phthalate and $HClO_4$ using Gran's method for strong acids and bases.⁶

The buffer solution (E_0 -solution) for the calibration of the electrode system was 0.01 and 0.09 M with respect to $HClO_4$ and $NaClO_4$, respectively.

Potentiometry. The potentiometric measurements were carried out on a locally constructed titration system consisting of a multichannel high-impedance amplifier, a Hewlett-Packard 3478A multimeter and a Metrohm 665 Dosimat piston burette. The equipment was controlled with an Amstrad PC 1640 HD 20 computer using the program TIT3.⁷ The electrode system consisted of an Orion 91-01sc glass electrode and an Orion 9002 Ag, AgCl(s) double-junction reference electrode. The titrations were carried out in a temperate room (25°C) in 0.10 M $NaClO_4$ solutions at $25.0 \pm 0.2^\circ C$.

Every titration was begun with the calibration of the electrode system by titration of 40–50 ml of the 0.1 M E_0 -solution with CO_2 -free 0.1 M NaOH solution. These data were employed using Gran's method to obtain the values of E_0 and E_j values in the Nernst equation [eqn. (1)]. The

$$E = E_0 + 59.16 \log h + E_j \quad (1)$$

liquid junction potential, E_j , was significant at $pH < 2.8$.

As the ligand can form two types of complexes, $[Ln(HL)_n]^{3-2n}$ and $[LnL_n]^{3-3n}$, two types of potentiometric measurements were performed to obtain the

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stability constants of the present lanthanoid(III) complexes. In the first series of titrations, the lanthanoid perchlorate solution was titrated directly with a buffered ligand solution, while in the second one, a mixture of lanthanoid perchlorate and ligand acid was titrated with 0.1 M NaOH solution.

In the first series the pH was maintained between 2.2 and 2.8, in which region the formation of $[\text{Ln}(\text{HL})_n]^{3-2n}$ complexes could be expected to be dominant. In these titrations 70–80% of the carboxylate protons of the ligand were neutralized in the buffered titrant solution. The total metal concentration, C_M , varied between 0.01 and 0.015 M.

The second series of titrations was carried out up to pH 8–9, in which range $[\text{LnL}_n]^{3-3n}$ complexes would also be expected to form. The total concentration of lanthanoid, C_M , varied from 0.002 to 0.008 M, while that of the ligand, C_L , from 0.005 to 0.015 M.

Calorimetry. The calorimetric titrations were performed on a Peltier-cooled calorimeter constructed in this laboratory. The calorimeter and the titration procedure used have been described in detail elsewhere.^{8,9}

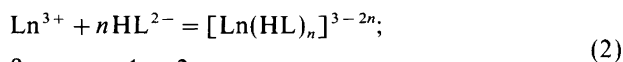
Lanthanoid(III) perchlorate solutions ($0.008 < C_M < 0.012$ M) were titrated with 1.2 ml aliquots of the buffered ligand solution ($C_L = 0.034$ M and $[\text{H}_2\text{L}^-] = 0.006$ – 0.01 M). The heats of dilution of the ligand and lanthanoid(III) concentrations were determined as described earlier.¹

Treatment of potentiometric and calorimetric data. For the acid constants of 3-bromo-5-sulfosalicylic acid, the values $\text{p}K_{a1} = 2.02$ and $\text{p}K_{a2} = 10.52$ were used for the calculations of the thermodynamic parameters.¹⁰ These correspond to deprotonation of the carboxylic and phenolic groups, respectively.

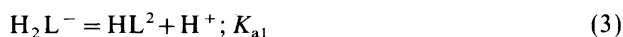
The stability constants of the lanthanoid(III) complexes were calculated from the potentiometric data with the program LETAGROP.^{11,12} The 'best fit' to the experimental data was determined by minimizing the error squares sum $U = \sum (H_{\text{calc}} - H_{\text{expl}})^2$, where H is the total hydrogen ion concentration. The hydrolysis of lanthanoid(III) ions was taken into account by assuming the constants reported in the literature.¹³

In order to visualize the relative amounts of the different species, the program SOLGASWATER¹⁴ was used to calculate distribution diagrams for the present equilibrium systems.

The ΔH values were calculated with a Simplex algorithm program written by W. Cacheris at Florida State University. In these calculations the deprotonation of the hydroxyl group of the ligand, and the hydrolysis of the lanthanoid ions, were neglected, since in each calorimetric titration the pH was always less than 3. The assumed equilibria were those of eqns. (2) and (3).



$$\beta_{1(11)_n}, n = 1 \text{ or } 2$$



¹³C NMR spectroscopy. The proton-decoupled ¹³C NMR spectra were recorded on a Bruker AM200 NMR spectrometer operating at 50.288 MHz for ¹³C. The spectral width was 10 kHz and the resolution 1.2 Hz/data point. The pulse width was 4 μs, corresponding to a nuclear tip angle of ca. 45°, and the relaxation delay was 4 s. The total accumulation time varied between 17 and 20 h, yielding a signal-to-noise ratio of ca. 10 for the quaternary carbon atoms after the application of an exponentially decaying window function. The uncertainty in the peak position (i.e. in the chemical shift measured relative to an arbitrary reference), based on the linewidths, signal-to-noise ratios and point resolution, is estimated to be ca. 0.1 ppm. D₂O was used as a lock substance.

Results

Figure 1 shows potentiometric data for the erbium(III)–3-bromo-5-sulfosalicylic acid system for the pH range 2.2–2.8 expressed as \bar{n} vs. $-\log [\text{HL}^{2-}]$ (\bar{n} = average number of ligand anions bound per metal cation). In this pH range the dominant ligand species is HL^{2-} , in which the sulfonate and carboxylate groups are ionized. As a result the stability constants, $\beta_{1(11)_n}$, for reactions (2) can be calculated from these data. Although it is obvious from the data that $[\text{Ln}(\text{HL})_2]^-$ is also formed, no stability constant for this species is reported, as the maximum \bar{n} values were too small (ca. 0.2) to allow valid estimates. Figure 1 also shows the agreement of experimental data with the \bar{n} values calculated from the $\log \beta_{1(11)}$ values obtained by the computer analysis.

The mathematical analysis of the potentiometric data in the range $3 < \text{pH} < 8$ –9 was started by making an $\bar{n}(-\log [\text{L}^{3-}])$ plot for each equilibrium system. In this pH region the complexing species L^{3-} is present together with the HL^{2-} species. In the higher pH region the potentiometric data cannot be explained solely by the

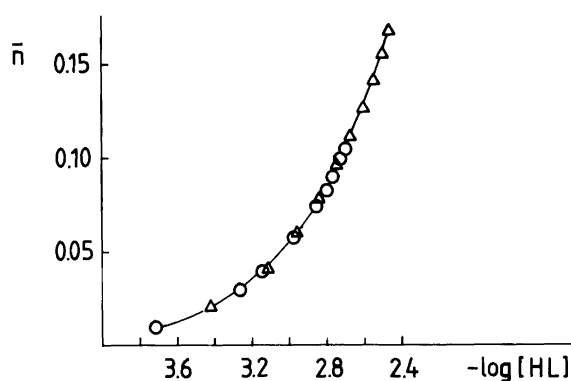


Fig. 1. Potentiometric data for the Er(III)–3-bromo-5-sulfosalicylic acid system obtained at $2.2 < \text{pH} < 2.8$ and plotted as \bar{n} vs. $-\log [\text{HL}^{2-}]$. The solid curve was calculated using $\log \beta_{1(11)} = 1.77$. Different symbols denote the following starting concentrations (mol/l): \circ , $C_M = 0.01269$ and $C_H = 0.00185$; \triangle , $C_M = 0.01269$ and $C_H = 0.0170$. Titrant: \circ , $C_L = 0.02979$ and $[\text{HL}^{2-}] = 0.00695$; \triangle , $C_L = 0.06138$ and $[\text{HL}^{2-}] = 0.01480$; $V_0 = 64.5$ ml in both cases.

Table 1. Results of a *pqr*-analysis for the potentiometric data with $\bar{n} > 1.2$ –1.4 performed for neodymium(III), gadolinium(III) and erbium(III) systems.^a

Ln(III)	$\log \beta_{1,-1,1}$	$\log \beta_{1,-1,2}$	$\log \beta_{1,-2,1}$	<i>U</i>
Nd	-1.0(5)	—	—	8.9
	—	3.7(6)	—	12.5
	—	—	-9.4(6)	10.9
	-1.1(7)	3.1–3.5	—	8.5
	-1.2(7)	—	-9.7–-9.45	7.4
Gd	-0.4(4)	—	—	5.5
	—	4.41(24)	—	3.2
	—	—	-8.71	3.9
	—	4.41(24)	-8.96	3.2
	-0.8(6)	—	-8.9(4)	2.5
	-8.9–-0.64	4.2(5)	—	2.6
Er	0.7(3)	—	—	15.0
	—	6.1(3)	—	16.5
	—	—	-6.9(3)	13.9
	0.4(6)	—	-7.2(6)	9.4
	0.4(6)	5.8(8)	—	10.8

^aData comprised three or four individual titrations with a total of about 100 potential readings. $C_L : C_M$ was varied between 2 and 3.5 in these titrations. Values in parentheses are three times the standard deviations.

formation of mononuclear LnL_n^{3-3n} species, as Fig. 2 demonstrates for the erbium(III)-3-bromo-5-sulfosalicylic acid system. For $\bar{n} < 1$, *n* is dependent both on the hydrogen ion and ligand anion concentrations, and \bar{n} does not attain any limiting values within the investigated area. This is a clear indication that some ternary hydroxo complexes and/or some lanthanoid hydrolysis products are formed in appreciable amounts. As a consequence, the data were divided into two parts, one with points with $\bar{n} < 1.0$ –1.2 (depending on the titration conditions), and another with $\bar{n} > 1.0$ –1.2. The assumption of two mononuclear complexes $[\text{LnL}]$ and $[\text{LnL}_2]^{3-}$ together with the protonated $[\text{Ln(HL)}]^+$ compound was confirmed when the computer calculation was performed on the data with $\bar{n} < 1.0$ –1.2.

Table 2. Stability constants for lanthanoid(III)-3-bromo-5-sulfosalicylic acid complexes as overall stability constants ($\text{Ln}^{3+} + \rho\text{H}^+ + r\text{L}^{3-} = \text{LnH}_\rho\text{L}_r^{3+\rho-3r}$) ($I = 0.10 \text{ M (NaClO}_4)$; $T = 25^\circ\text{C}$).^a

Ln(III)	$\log \beta_{1,1,1}$	$\log \beta_{1,0,1}$	$\log \beta_{1,0,2}$	$\log \beta_{1,-1,1}$	$\log \beta_{1,-2,1}$
La	12.30(4)	6.49(5)	10.72(17)	-2.73(24)	-11.85(16)
Pr	12.34(3)	6.84(4)	11.70(9)	-1.75(20)	-10.31(19)
Nd	12.36(1)	6.86(4)	11.61(7)	-1.16(24)	-9.70(27)
Sm	12.48(5)	7.39(4)	12.39(12)	-0.35(16)	-8.18(13)
Eu	12.46(3)	7.60(4)	13.02(9)	-0.09(16)	-8.49(19)
Gd	12.38(4)	7.40(4)	12.35(12)	-0.54(13)	-9.22(18)
Tb	12.42(3)	7.47(8)	12.61(18)	—	-8.25(25)
Dy	12.28(3)	7.58(5)	12.85(10)	—	-8.42(18)
Ho	12.38(3)	7.64(6)	13.09(12)	—	-7.71(18)
Er	12.30(3)	7.72(5)	13.19(17)	0.36(16)	-7.17(16)
Tm	12.34(1)	7.69(4)	13.24(10)	—	-7.15(15)
Yb	12.39(5)	7.83(6)	13.66(18)	—	-6.40(16)
Lu	12.33(1)	7.56(8)	13.42(11)	0.42(26)	-6.85(25)

^aValues in parentheses are three times the standard deviations.

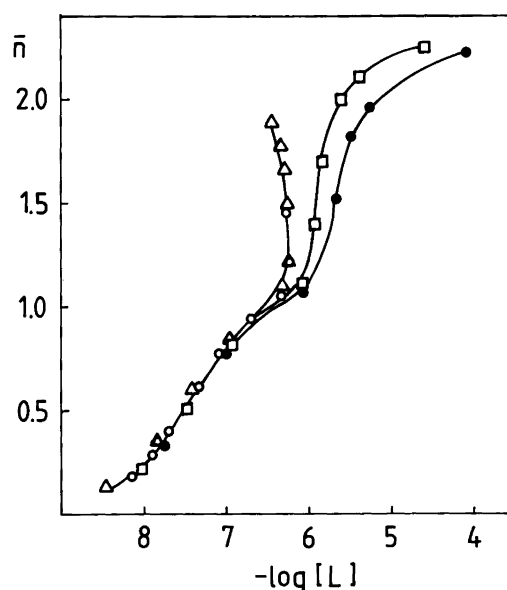


Fig. 2. Part of the experimental data ($3 < \text{pH} < 8$) plotted as \bar{n} vs. $-\log [\text{L}^{3-}]$ for the Er(III)-3-bromo-5-sulfosalicylic acid system. Different symbols denote the following starting concentrations (mol/l) in the titration cup: ●, $C_M = 0.00315$ and $C_L = 0.0127$; □, $C_M = 0.00341$ and $C_L = 0.00940$; Δ, $C_M = 0.00471$ and $C_L = 0.00977$.

The data with $\bar{n} > 1.0$ –1.2 were analyzed by a systematic testing of the formation of different hydroxo complexes. The calculations were performed with the hypotheses that only one or two new complexes $[\text{Ln}_q(\text{OH})_w\text{L}_r]$ are present. The values obtained for

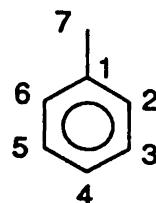


Fig. 3. Numbering of carbon atoms in benzoic acid ligands.

Table 3. Calorimetric titration data for the Dy(III)–3-bromo-5-sulfosalicylic acid system [$I = 0.10$ M (NaClO_4); $T = 25^\circ\text{C}$].

Titration	Titrant vol./ml	$Q(\text{corr})^a/\text{mJ}$	$Q(\text{calc})/\text{mJ}$	$[M]/\text{mM}$	$[\text{H}_2\text{L}^-]/\text{mM}$	$-\log h$
Titration 1 ^b						
1.2	75.4	68.7	6.490	0.573	3.224	
2.4	142.7	130.3	6.157	1.222	3.123	
3.6	189.1	185.7	5.856	1.649	3.051	
4.8	224.7	236.1	5.583	2.155	2.996	
Titration 2 ^c						
1.2	26.4	40.1	6.228	0.583	3.315	
2.4	80.2	76.5	5.903	1.149	3.263	
3.6	127.7	109.7	5.608	1.699	3.224	
4.8	132.5	140.1	5.339	2.232	3.193	
6.0	164.1	167.9	5.091	2.750	3.167	

^a Corrected for dilution effect. ^b Initial conditions: cup solution (solution to be titrated), volume 50.0 ml, $C_M = 0.006586$ M, $C_H = 0.000412$ M; titrant, $C_L = 0.03491$ M, $C_H = 0.009796$ M. ^c Initial conditions: cup solution, 50.0 ml, $C_M = 0.006586$ M, titrant, $C_L = 0.03483$ M, $C_H = 0.004735$ M.

the stability constants of the $[\text{LnL}]$ and $[\text{LnL}_2]^{3-}$ complexes were kept as non-variable parameters in these calculations. The results of this analysis for neodymium(III), gadolinium(III) and erbium(III) are given in Table 1. The lowest value of U was obtained in each case with the model consisting of the species $[\text{Ln}(\text{OH})\text{L}]^-$ and $[\text{Ln}(\text{OH})_2\text{L}]^{2-}$. However, the values given should be regarded as tentative constants for these complexes owing to the small stability in the potential readings in this pH region. This can also be seen in relative large U -values obtained for the different models.

The complete description of the complexation is given by the species $[\text{LnHL}]^+$, $[\text{LnL}]$, $[\text{LnL}_2]^{3-}$, $[\text{Ln}(\text{OH})\text{L}]^-$ and $[\text{Ln}(\text{OH})_2\text{L}]^{2-}$, and Table 2 lists the calculated values, performed on all the data, for $\log \beta_{1(11)}$, $\log \beta_{1,0,1}$, $\log \beta_{1,0,2}$, $\log \beta_{1,-1,1}$ and $\log \beta_{1,-2,1}$.

A typical set of calorimetric data is presented in Table 3. In these titrations, only the protonated com-

Table 4. Thermodynamic parameters for formation of $[\text{Ln}(\text{HL})]^+$ complexes and protonation of 3-bromo-5-sulfosalicylic acid [$I = 0.10$ M (NaClO_4); $T = 25^\circ\text{C}$].

Ln(III)	$\log \beta_{1(11)}^a$	$-\Delta G_{1(11)}^a/\text{kJ mol}^{-1}$	$\Delta H_{1(11)}^b/\text{kJ mol}^{-1}$	$\Delta S_{1(11)}^b/\text{J}(\text{mol K})^{-1}$
La	1.77(4)	10.1(1)	2.2(2)	41(1)
Pr	1.81(3)	10.3(1)	0.9(4)	38(1)
Sm	1.95(5)	11.1(1)	2.3(2)	45(1)
Gd	1.85(4)	10.6(1)	3.8(2)	48(1)
Dy	1.75(3)	10.0(1)	4.6(1.0)	49(3)
Er	1.77(3)	10.1(1)	2.2(3)	41(1)
Yb	1.86(5)	10.6(1)	3.9(1.0)	49(3)
H	2.02(1)	11.53(3)	-1.2(1)	34(1)

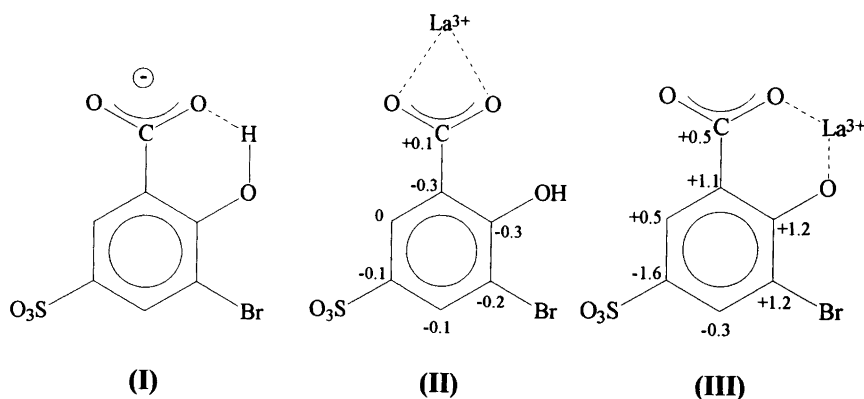
^a Three times the standard deviation. ^b Based on repetitive titrations.

plexes of eqn. (2) form. However, the uncertainties in $\log \beta_{1(11)}$ and the corresponding $\Delta H_{1(11)}$ are so large that they are not given. Table 4 gives the thermodynamic parameters for the formation of $[\text{Ln}(\text{HL})]^+$. The standard deviations in the individual titrations for $\Delta H_{1(11)}$ were 0.1–0.2. The errors given in Table 3 are based on the agreement in repetitive titrations.

The numbering of carbon atoms in benzoic acid ligands is shown in Fig. 3. ^{13}C chemical shift differences of each carbon atom between free 3-bromo-5-sulfosalicylate ligand and coordinated species at various pH values are shown in Fig. 4.

Discussion

The dependence of $\log \beta_1$ ($\log \beta_{1(11)}$ in the case of hydroxycarboxylic acids) on the acidity of the carboxylic acid group of alkyl and aryl monocarboxylate ligands in lanthanoid(III) coordination species is presented for a number of La(III) complexes in Fig. 5. The value for the 3-bromo-5-sulfosalicylate species $[\text{La}(\text{HL})]^+$ falls on a common line for various aromatic sulfo-substituted *o*-hydroxycarboxylate ligands. On the basis of thermodynamic parameters, the enhanced stability of

**Fig. 4.** ^{13}C chemical shift differences between the free 3-bromo-5-sulfosalicylic acid ligand (HL^{2-}) and that coordinated to lanthanum $\{[\text{La}(\text{HL})]^+$ and $[\text{LaL}]\}$.

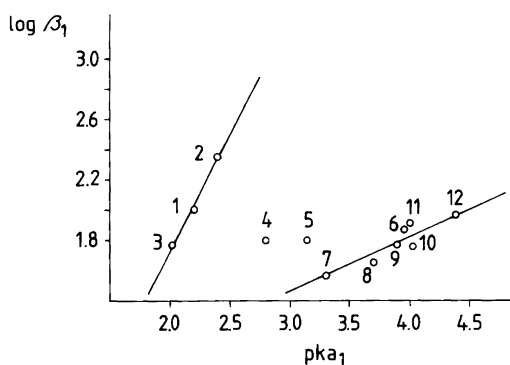


Fig. 5. Relationship between the stability constant of La(III) $\log \beta_{1(11)}$ for *o*-hydroxycarboxylates or $\log \beta_{1(01)}$ for benzoates, and the acid constant, pK_{a1} , of the carboxylic group of the ligand. (1) 1-hydroxy-4,7-disulfo-2-naphthoic acid,⁴ (2) 5-sulfosalicylic acid,¹⁵ (3) 3-bromo-5-sulfosalicylic acid,⁴ (4) 2,5-dihydroxybenzoic acid,⁵ (5) 2,4-dihydroxybenzoic acid,⁵ (6) 4-fluorobenzoic acid,² (7) 3-nitrobenzoic acid,² (8) 3-fluorobenzoic acid,² (9) 3,5-dihydroxybenzoic acid,⁵ (10) 3-hydroxybenzoic acid,³ (12) 4-hydroxybenzoic acid.³

the $[\text{Ln}(\text{HL})]^+$ complexes in the lanthanoid(III)–5-sulfosalicylic acid system has been attributed to the formation of a chelate structure, involving the carboxylate and phenolic groups of the ligand.^{15–17} However, in the case of 2,4- and 2,5-dihydroxybenzoic acids the ^{13}C NMR spectroscopic data could also be interpreted without chelate formation in the corresponding $[\text{Ln}(\text{HL})]^{2+}$ complexes.⁵ Instead, the higher stability of the salicylato complexes was explained by the mesomeric effect of the hydroxyl group in the *ortho*-position to the carboxylic acid group. It has also been suggested that sulfonic acid groups can stabilize the complex by an outer-sphere electrostatic attraction.¹⁸

Because of the fast exchange of the complexed and the free ligand, the observed chemical shifts are concentration-weighted averages between these two chemical environments. Figure 6 shows the pH dependence of the relative concentrations of the coordinated and non-

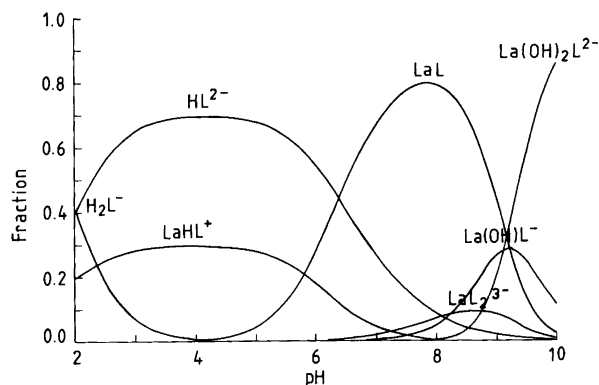


Fig. 6. The pH dependence of the relative concentrations of the coordinated and noncoordinated species in the La(III)–3-bromo-5-sulfosalicylic acid system at $I = 0.1 \text{ M NaClO}_4$ and 25°C . $C_M = C_L = 0.010 \text{ mol/l}$.

coordinated species in the La(III)–ligand system. The ^{13}C NMR spectra were recorded at the pH values of 4.0, 5.8 and 7.0. The two acid constants of the free ligand ($pK_{a1} = 2.02$ and $pK_{a2} = 10.52$) indicate that only HL^{2-} exists in solution in the pH range 4–7.

Upon complex formation, the resonance due to C(7) shifts downfield (decreased shielding), indicating a loss of electron density from the carboxyl oxygens to the lanthanum ion (Fig. 4). This shift increases as a function of pH. However, there is a significant difference in the behaviour of the other ligand carbon signals. At pH 4 the resonances of C(1)–C(5) are shifted upfield (increased shielding) upon complexation [C(6) shows no significant change]. At pH 5.8 the signals due to C(1)–C(3) and C(6) are shifted downfield, and those due to C(4) and C(5) upfield. This can be explained upon examination of distribution diagram of Fig. 6.

At pH 4 the solution contains ca. 70% HL^{2-} and 30% $[\text{La}(\text{HL})]^+$. The small upfield shifts of the C(1)–C(3) signals indicate that the intramolecular hydrogen bond from the hydroxyl hydrogen to the carboxyl oxygen is broken upon formation of the $[\text{La}(\text{HL})]^+$ complex. However, at pH 5.8 the solution contains 60% of HL^{2-} and about 20% of both complexes $[\text{La}(\text{HL})]^+$ and $[\text{LaL}]$. Downfield shifts of the average signals due to C(1)–C(3) and C(6) can be rationalized by assuming that, in contrast to $[\text{La}(\text{HL})]^+$, the complex $[\text{LaL}]$, in which the hydroxyl group is deprotonated, has a clear chelate structure involving both the carboxyl and hydroxyl oxygens.

Figure 7 shows the variation of the thermodynamic parameters of formation of $[\text{Ln}(\text{HL})]^+$ complexes of 3-bromo-5-sulfosalicylic acid and 5-sulfosalicylic acid. From the similar shapes of the curves for these two series of complexes it can be inferred that the complexation involves similar dehydration and bonding effects in both systems. The stability constants of α -hydroxycarboxylato complexes are comparable to those of 3-bromo-5-sulfosalicylato and 5-sulfosalicylato complexes, but the enthalpies and entropies of complexation are rather

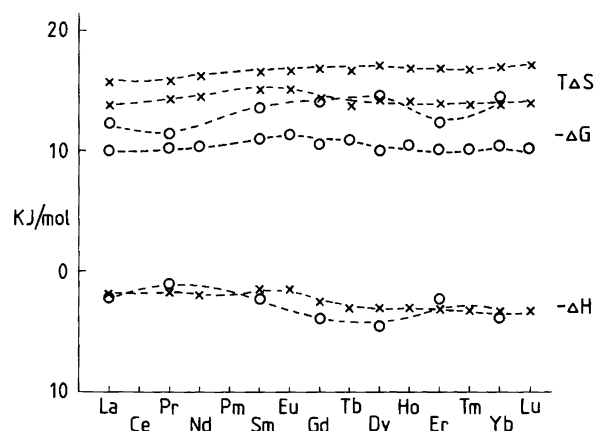


Fig. 7. Thermodynamic parameters (ΔG , ΔH and ΔS) for formation of Ln(III) complexes of 3-bromo-5-sulfosalicylic acid (O) and 5-sulfosalicylic acid (X).

Table 5. ^{13}C Chemical shift data of 3-bromo-5-sulfosalicylate as free ligand (HL^{2-}) and as coordinated to lanthanum(III) $\{[\text{La}(\text{HL})]^+$ and $[\text{LaL}]\}$.

Species	pH	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
HL^{2-}	5.8	-9.4	32.4	-17.5	5.5	5.3	-1.0	45.3
$\text{La}^{3+}/\text{HL}^{2-}$	4.0	-9.7	32.1	-17.7	5.4	5.2	-1.0	45.4
$\text{La}^{3+}/\text{HL}^{2-}$	5.8	-8.3	33.6	-16.3	5.2	3.7	-0.5	45.8

different. For example, $\Delta H_{1(11)}$ and $\Delta S_{1(11)}$ values for the europium(III)-monolactato complexation at 2 M ionic strength, and samarium(III)-3-bromo-5-sulfosalicylate complexation at 0.1 ionic strength are -8.0 and 2.3 kJ mol^{-1} , and 21 and 45 J (mol K)^{-1} respectively.¹⁵ The data for the lanthanoid(III)-lactate system were interpreted as indicating the inclusion of a water molecule between the Ln^{3+} ion and the hydroxyl group.¹⁹ The ΔH and ΔS values for the samarium(III)-benzoato and samarium(III)-3-fluorobenzoato complexation at 0.1 ionic strength are 7.6 and 6.1 kJ mol^{-1} , and 68 and 58 J (mol K)^{-1} , respectively. Both the enthalpy and entropy values for the lanthanoid(III) complexation with aromatic ligands containing hydroxyl and carboxyl groups in positions *ortho* to each other are about the same order of magnitude, and fall between the corresponding values of various aliphatic α -hydroxycarboxylic acid and aromatic *o*-hydroxycarboxylic acid systems.

The heat of protonation of the carboxylic acid group of 3-bromo-5-sulfosalicylic acid is of the same magnitude as those of the corresponding hydroxycarboxylic acids reported in the literature (Table 5).¹⁻⁵

The stability constants of the $[\text{LnL}]$ complexes in which the hydroxyl group is also deprotonated are much larger than the corresponding stability constants of the $[\text{Ln}(\text{HL})]^+$ complexes, which is also an indication of the chelate structure in $[\text{LnL}]$. The variation of $\log \beta_{101}$ values with lanthanoid atomic number shows a tetrad effect,^{20,21} whereas $\log \beta_{1(11)}$ shows no such correlation.

The pattern (and tetrad effect) of $\log \beta_{101}$ is quite similar to that of the other aromatic *o*-hydroxycarboxylate complexes.^{4,22}

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