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Determination of Stability Constants of Mixed Ligand Complexes of the Lanthanum(III) Ion and Identification of Structures

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ABSTRACT: In this study, the stability constants of a mixed ligand complex of lanthanum(III) ion by using ethylenediaminetetraacetic acid (EDTA, H_2A) as a primary ligand and 2,3-dihydroxybenzoic acid (2,3-DHBA, H_3B) as a secondary ligand have been investigated. The stability constants of the binary and mixed ligand complexes have been determined by using a potentiometric method and the BEST computer program at 25 °C, in a 0.1 M NaCl ionic medium. In addition, the identified ternary complex by potentiometry was isolated as a solid, and the structural characteristics have been examined using IR, NMR, elemental analysis, differential thermal analysis, thermogravimetric analysis, and the conductivity method.

INTRODUCTION

The term lanthanides when strictly defined refers to the 14 elements following lanthanum in the periodic table. Lanthanum and rare earth elements (lanthanide-Ln) are Group 3 elements.[1] The coordination behavior of the lanthanide elements is interesting because of the relatively high charge density of the cations, the strongly electrostatic nature of their bonding, and the variety of coordination numbers attained in different complexes.[2] Lanthanide cations behave as hard Lewis acids and bind most strongly to hard bases such as oxygen, thus explaining their high affinity for water. Successful complexing agents frequently involve multiple lanthanide-oxygen bonds. Because of their high coordination numbers lanthanides commonly have water molecules remaining in their primary coordination sphere even when complexed with a polyfunctional ligand such as aminopolycarboxylates.[2] Lanthanides typically have 8 to 9 waters of hydration in their inner coordination shell, some of which are displaced upon complexation.[3] La(III) has the biggest ionic radius (1.17 Å) of the lanthanide(III) ions, with a coordination number of 8 to 10. The addition of a second ligand can result in formation of a ternary complex with the displacement of the remaining waters of hydration. The complexation of lanthanides with carboxylate ligands to form ternary complexes with the total displacement of H_2O has been studied less than the formation of binary complexes.[4]

Ethylenediaminetetraacetic acid (EDTA, H_2A) is a polyamino carboxylic acid, and it can act as a hexadentate ligand. The interaction of La(III) with EDTA has been studied by many researchers.[5−9] These studies calculated the stability constant and thermodynamic parameters of the La(III):EDTA complex in various ionic media and at various temperatures. Some researchers reported that La(III) has ten-coordination in the EDTA complex.[10]

Dihydroxybenzoic acids are very interesting ligands, since they have a bidentate catechol part and one carboxylate oxygen. 2,3-Dihydroxybenzoic acid (2,3-DHBA, H_3B) contains three potential binding sites on three adjacent ring carbons; only two of these groups in each ligand can lose protons in the measurable pH range, due to the formation of intramoleculer hydrogen bonds between the $-COO^-$ and phenolic $-OH$ groups. It is a good model of competitive salicylate (CO_2^-, O^-) and catecholate type (O^-, O^-) chelation in the same molecule (Figure 1).[11,12] Sahoo et al. investigated the complexes of La(III) with 2,3-DHBA at 25 °C and in a 0.1 M KCl ionic medium through potentiometric and spectroscopic methods, and they determined the stability constants of LaB and $LaB(HB)^{2-}$ (where B is 2,3-DHBA) complexes as 10.54 and 13.57, respectively.[13] Kula et al. described the complex of La(III) with 2,3-DHBA and the solubility in water by IR and X-ray spectra, and the thermal decomposition in an air atmosphere of LaB complex was investigated. The LaB complex as obtained was anhydrous and an amorphous solid of a gray-beige color, with a molar ratio of metal to organic ligand of 1:3 and a general formula of $La[C_6H_3(OH)_2COO]_3$.[14]

Besides simple coordination species like binary systems consisting of single type metal ion and single type ligand in organisms and ecosystems, a large number of chemical equilibria include coordination species containing more than one metal ion and/or more than one ligand type takes place. Consequently, mixed ligand studies have become more important recently to describe these systems and to contribute to application of the complexes for various purposes.[15]

Although there are studies on binary systems produced by EDTA and 2,3-DHBA with the La(III) ion in the literature, there is no study on the mixed complexes with these two ligands. Therefore, in this study, the protonation constants of EDTA and 2,3-DHBA and the stability constants of the binary and mixed ligand complex that these ligands form with La(III) were investigated in aqueous solution, and the mixed ligand complex was isolated in the solid state and characterized.

EXPERIMENTAL SECTION

Chemicals. All chemicals were of analytical grade and were used without further purification. Lanthanum oxide (La_2O_3, 99 %)

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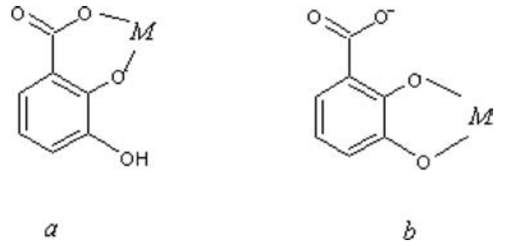


Figure 1. Coordination models of 2,3-DHBA: (a) salicylate type, (b) catecholate type.

Table 1. Protonation Constants ($\log K \pm \sigma^{x}$)^{y} of EDTA and 2,3-DHBA at Ionic Strength I = 0.1 M NaCl and 25 °C[a]

ligand	$\log K_1$	$\log K_2$	$\log K_3$
EDTA	9.48 ± 0.05	6.06 ± 0.04	-
	10.17[21]	6.11[21]	-
2,3-DHBA	12.20 ± 0.40	10.00 ± 0.20	2.72 ± 0.21
	>14[21]	9.81[22]	3.32[22]
		9.91[23]	2.74[23]

[a] x: standard deviation; y: ± 95 % confidence interval.

and the disodium salt of ethylenediaminetetraacetic acid (Na_2-EDTA, 99 %) were purchased from Merck, and 2,3-DHBA (97 %) was purchased from Sigma. The purities of the ligands were checked by potentiometry.[16] A stock solution of La(III) was prepared by dissolving the proper amount of lanthanum oxide (Sigma, 99.9 %) in a small excess of HCl (Merck, 37 % purity) to prevent hydrolysis. The concentration of free acid in the stock solution was systematically checked by potentiometric titration before each series of experiments. The stock solution of La(III) was standardized complexometrically by EDTA titration using the method by Schwarzenbach and Flaschka.[17]

Apparatus and Procedure. Potentiometric titrations were performed on a Schott Titroline Alpha Plus automatic titrator with a combined pH electrode (Schott), which was connected to a computer. All titrations were carried out in a double-walled glass cell. The temperature was maintained constant inside the cell at (25.0 ± 0.1) °C, by circulating water from an external thermostat (VWR, precision ± 0.1 °C). The pH meter was calibrated daily using standard buffer solutions (Merck) with pH values of 4.01, 6.96, and 8.96 at 25 °C. The combined glass electrode calibration was carried out daily from the titration of a strong acid (HCl, 0.1 M) with a strong base (NaOH, 0.1 M) at the same ionic strength before each titration to obtain the hydrogen ion concentration directly, so that p[H] was defined as $-\log[H^+]$.[18] This is because the emf values (E) depend on $[H^+]$ according to $E = E° + s\log[H^+] + J_H[H^+] + J_{OH}[OH^-]$, where J_H and J_{OH} are fitting parameters in acidic and alkaline media for the correction of experimental errors, mainly due to the liquid junction and to the alkaline and acidic errors of the glass electrode. The ionic strength of the solutions were adjusted to 0.1 M by NaCl,[19] and a total volume of 50 mL was used for each titration. Potentiometric titrations were carried out using three different metal concentrations [$(2.0 \cdot 10^{-3}, 3.0 \cdot 10^{-3}$, and $4.0 \cdot 10^{-3})$ M]. The experimental procedure involved the potentiometric titrations of the following solutions.

(a) 5 mL of 0.1 M HCl + 5 mL of 1 M NaCl (for cell calibration);
(b) 5 mL of 0.1 M HCl + 0.1 mmol of ligand A or B + 5 mL of 1 M NaCl (for the determination of protonation constants of ligands);
(c) Solution b + 10 mL of 0.01 M La(III) (for the determination of stability constants of MB or MA complexes);
(d) Solution a + 0.1 mmol of ligand A + 0.1 mmol of ligand B + 10 mL of 0.01 M (0.1 mmol) La(III) (for the determination of stability constants of MBA mixed ligand complex).

Grade A glassware and doubly distilled water were used throughout the measurements. Each experimental run consisted of obtaining equilibrium data throughout the pH range 4.00 to 11.00, as a function of millimoles of the standard 0.1 M base.

The spectroscopic study was performed using a GBS Cintra 303 model UV−visible spectrophotometer. Spectra of solutions containing 2,3-DHBA, (1:1) La(III):2,3-DHBA, and (1:1:1) La(III):EDTA:2,3-DHBA were taken separately between pH 3.5 and 10.5 within the (190 to 400) nm wavelength interval.

■ CALCULATIONS

To calculate the stability constants of binary and mixed ligand complexes, the data for the potentiometric titrations were treated by the microcomputer program BEST.[20] This comprises the best reaction model and applies the criterion for which species are present in equilibria, computes the concentrations of H^+ for each equilibrium and the quantity of the added base. Then, the stability constants of binary and mixed ligand complexes were calculated (Table 1). All of the protonation, binary, and ternary system titrations contained at least 99 experimental points between pH 2 and 10. The species distribution diagrams were obtained using the SPE program;[20] thus, the species existing in the La(III):EDTA:2,3-DHBA system are available.[20]

Preparation of the Mixed Ligand Complex. La_2O_3 is dissolved with concentrated HCl to prepare a La(III) solution. The EDTA and 2,3-DHBA ligands are added to the prepared La(III) solution in equal millimolar concentrations. The pH of the solution is adjusted to 9 with NaOH and mixed for a day. The obtained green solution is left for crystallization. Brilliant green crystals are obtained from the green complex solutions; however, they turn into a green powder in the course of time with the effect of light. This indicates that crystal waters with weak bonds exist in the structure of the complex, and these waters leave the crystal structure as a result of the effect of light and air over a short time. The complex is dissolved only in water. The melting point is 350 °C (decomposition), and the efficiency was 73 % (0.81 g).

■ RESULTS AND DISCUSSION

Potentiometric Method. *Protonation Constants of Ligand.* The protonation constants of EDTA and 2,3-DHBA was redeterminated by the potentiometric method at 25 °C and in a 0.1 M ionic medium (NaCl). The potentiometric titration curves were drawn from the obtained data (Figure 2, curves a and b). Only a single inflection point was observed in the titration curves of the ligands. In the potentiometric titration curve of 2,3-DHBA, the number of titrated protons is 1 per ligand. 2,3-DHBA has two deprotonable phenolic hydroxyls and one carboxylate proton. In previous studies, many researchers have reported that the first ionizing proton is a carboxylate, the second is a meta-position, and the third proton is an ortho-position phenolic hydroxyl.[12,23] The protonation constants of EDTA and 2,3-DHBA were

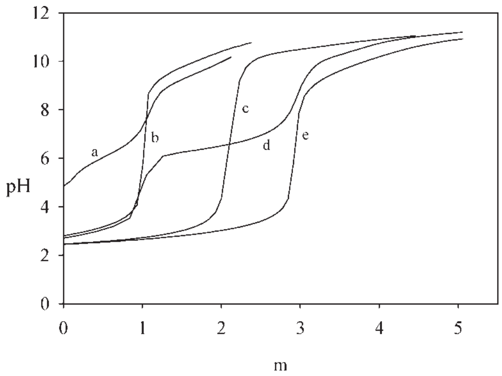


Figure 2. Potentiometric titration curves of La(III)/EDTA/2,3-DHBA system at 25 °C and $I = 0.1$ M NaCl; (a) EDTA alone; (b) 2,3-DHBA alone; (c) La(III)/EDTA (1:1); (d) La(III)/2,3-DHBA (1:1); (e) La(III)/EDTA/2,3-DHBA (1:1:1).

Table 2. Stability Constants $(\log \beta(K) \pm \sigma^x)^y$ of Binary and Mixed Ligand Complexes of La(III) at Ionic Strength $I = 0.1$ M NaCl and 25 °C[a]

$\log \beta_{LaA}$	$\log \beta_{LaB}$	$\log \beta_{LaH_2B}$	$\log K_{LaBH-1}$	$\log {K_{MAB}}^{MA}$	$\log \beta_{LaAB}$
14.60 ± 0.30	12.10 ± 0.30	2.45 ± 0.80	1.59 ± 0.11	5.22 ± 0.48	19.82 ± 0.48
15.40[5]	10.54[12]	-	-	-	-
14.72[6]					
16.91[7]					
15.88[8]					
14.48[21]					

[a] x: standard deviation; y: ± 95 % confidence interval.

recalculated from potentiometric data by the BEST program. The agreement between the present data is very good with the earlier results[21−23] (Table 1).

Complex of La(III) with EDTA. According to the titration curve for the La(III)/EDTA system at a mole ratio of (1:1), a inflection point is seen at $m = 2$ (Figure 2, curve c). The fact that the inflection point is at $m = 2$ may suggest that two protons pass into the solution when EDTA reacts with La(III), and as a result, a LaA (where A is EDTA) coordination compound is produced between La(III) and EDTA. It is possible to show the formation reaction and the stability constant equation of the LaA binary complex with eq 1.

$$La^{3+} + A^{4-} \rightleftharpoons LaA^{-} \qquad \beta_{LaA} = \frac{[LaA]}{[La][A]} \tag{1}$$

The stability constant for the LaA complex was determined by the BEST computer program according to the potentiometric data; the agreement was very good with earlier results[5−9,22] (Table 2) According to the distribution curve drawn for the La(III)/EDTA system (Figure 3a), the LaA type complex is produced at approximately 90 % of the La(III) at pH 2.

Complex of La(III) with 2,3-DHBA. The potentiometric titration was carried out in (1:1) mole ratios of La(III) to 2,3-DHBA over the pH range 3 to 10. The potentiometric titration curve was drawn with the obtained data (Figure 2, curve d). An inflection point at $m = 1$ is seen on the titration curve drawn for 2,3-DHBA alone. There are two inflection points on the potentiometric titration curve drawn for the La(III):2,3-DHBA system at $m = 1$ and $m = 3$. The formation reaction and the stability constant equation of the LaB (where B is 2,3-DHBA) binary complexes are shown with eqs 2 and 3.

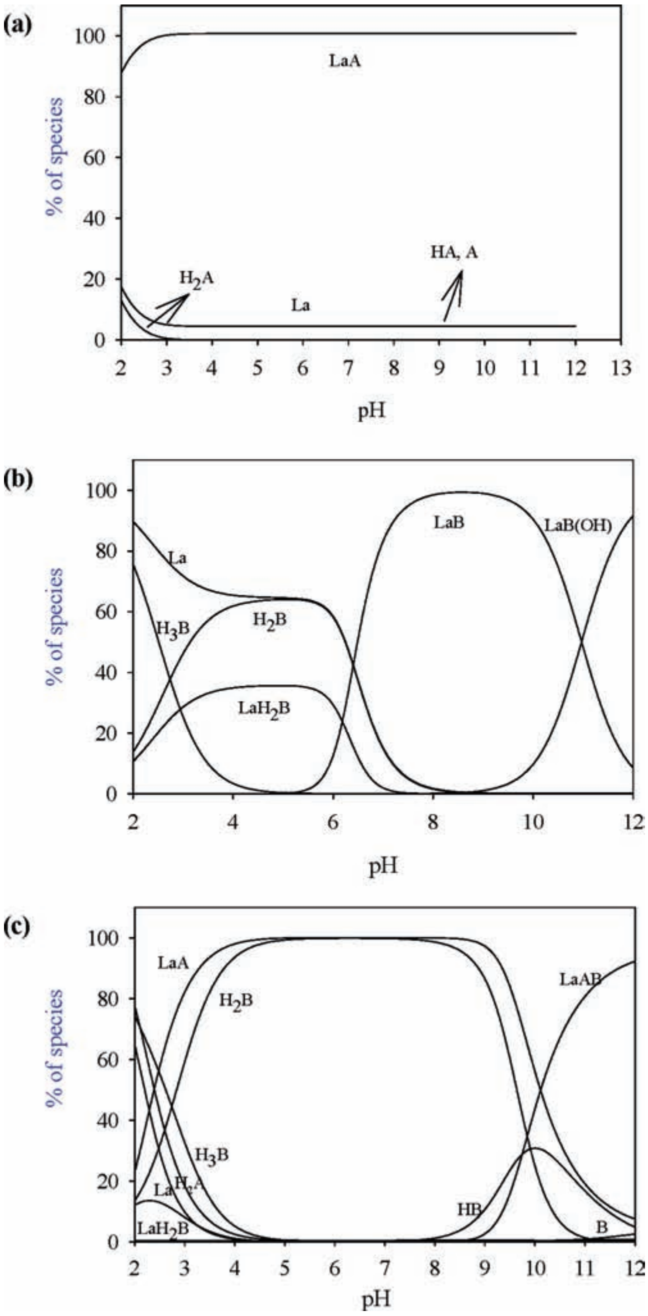


Figure 3. Distribution diagrams of La(III)/EDTA/2,3-DHBA system (a) La(III)/EDTA (1:1), (b) La(III)/2,3-DHBA (1:1), (c) La(III)/EDTA/2,3-DHBA (1:1:1).

$$La^{3+} + H_2B^{-} \rightleftharpoons LaH_2B^{2+} \qquad \beta_{LaH_2B} = \frac{[LaH_2B]}{[La][H_2B]} \tag{2}$$

$$La^{3+} + B^{3-} \rightleftharpoons LaB \qquad \beta_{LaB} = \frac{[LaB]}{[La][B]} \tag{3}$$

The stability constant for the LaB and LaH_2B^{2+} complexes were determined by the BEST computer program according to the

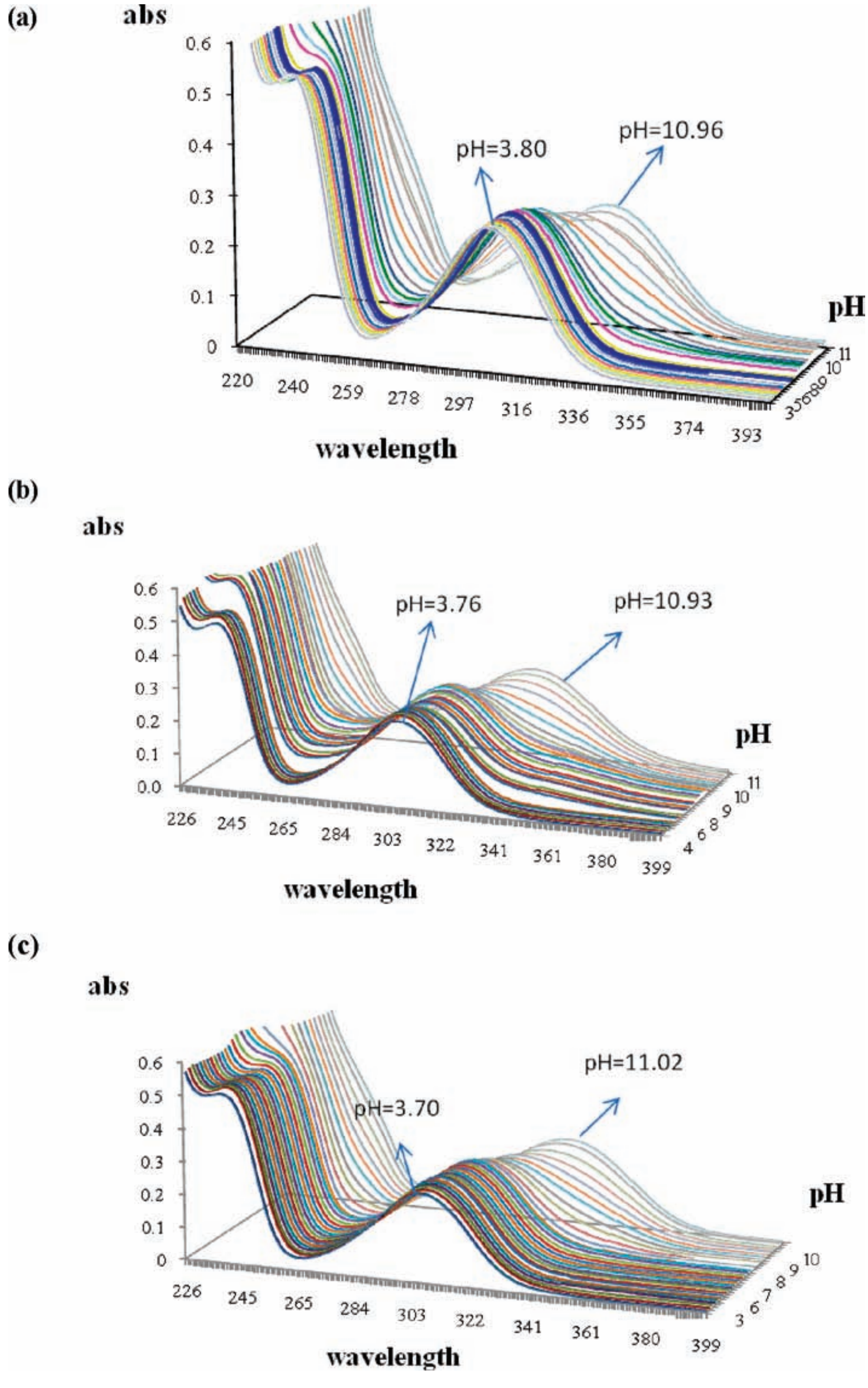


Figure 4. Spectra of La(III)/EDTA/2,3-DHBA system at different pH (a) 2,3-DHBA alone, (b) La(III)/2,3-DHBA (1:1), (c) La(III)/EDTA/2,3-DHBA (1:1:1).

potentiometric data (Table 2). The distribution curve is drawn for the La(III)/2,3-DHBA system by the SPE program (Figure 3b). It is seen that the LaH_2B complex is present at approximately 30 % between pH 3.5 and 6.0. The LaB complex starts to form after pH 6.0, and the maximum concentration of LaB is 90 % at ca. pH > 8. It can be said that the coordination of 2,3-DHBA to La(III) is a carboxylate type (COO^-, O^-) in acidic pH range and catecholate type (O^-, O^-) after pH 8.0.

Mixed Ligand Complex of La(III). Two possible explanations[24,25] for the formation of mixed ligand complexes of La(III) must be considered: (1) if the coordination number of La(III) is six, the secondary ligand either displaces one or more coordinated groups of the primary ligand (EDTA, HEDTA, or NTA) (as well as a molecule of water); or (2) if the coordination number of La(III) is larger than six, the mixed ligand complex formation occurs without the displacement of coordinated groups. In the absence of definitive structure studies, it is, of course, impossible to make an absolute choice between the two alternatives. A comparison of the titration curves of the binary and ternary systems may be helpful.

Potentiometric titrations of the (1:1:1) mole ratio La(III)/EDTA/2,3-DHBA system were performed in I = 0.1 M NaCl ionic medium and at 25 °C. In the mixed ligand system, one inflection point was observed at m = 3.0. In comparison with the titration curves of 2,3-DHBA for the La(III)/EDTA/2,3-DHBA system (Figure 2, curve b and e) a decrease in pH is seen. The decrease in pH indicates that a LaAB complex has been formed. The formation reactions and overall stability constant of LaAB complex in the La(III)/EDTA/2,3-DHBA system have been shown by eq 4.

$$La^{3+} + A^{4-} + B^{3-} \rightleftharpoons LaAB^{4+}$$

$$\beta_{LaAB}^{La} = \frac{[LaAB]}{[La][A][B]} \tag{4}$$

The stability constants of the LaAB complex are listed in Table 2. According to the distribution curve of La(III)/EDTA/2,3-DHBA system (Figure 3c), the LaAB complex began to form around pH~9 and is present at approximately 85 % at pH 11.

Spectroscopic Results. The recorded electronic spectra of the 2,3-DHBA at different pH = 3.5 to 10.5 are shown in Figure 4a. The whole spectra is presented in two sets according to the ligand peak at 306 nm (pH = 3.80) and shifted hydrochromically to 304.9 nm, whereas with an increase in pH from 5.03, the peaks at 304.9 nm start to shift bathochromically. The first blue shift happened due to the conversion of the COOH group into a COO^- ion, whereas the red shift was assigned (pH = 10.3, λ_{max} = 317.4 nm) to the deprotonation of the hydroxyl group.[13]

Table 3. IR Spectrum Data of Ligands and Mixed Ligand Complex

	frequency/cm^{-1}				
	ν_{H_2O}	ν_{O-H}	$\nu_{C-H(arom)}$	$\nu_{C-H(aliph)}$	$\nu_{C=O}$
EDTA	-	3381.5	-	3027.0	1674
2,3-DHBA	-	3368.4	3047.3	-	1678.2
LaAB Complex	3000−3500	-	2962.1	2909.0	1658.6

The spectra of the solutions containing La(III)/2,3-DHBA and La(III)/EDTA/2,3-DHBA are taken between pH 3.70 and 11.0 within the (190 to 400) nm wavelength interval (Figure 4b and c). It is seen that wavelength peak shifts to red in the spectra taken after pH 7.0. This shifting to red in the spectra indicates that the ligand is bound by the catecholic oxygen to form the binary and mixed ligand complex.

Mixed Ligand Complex La(III) Ion and Identification of Structure.

IR Results. Coordination and/or crystal waters exist in the structure of the obtained complex. Because the (3000 to 3500) cm^{-1} region was overlapped by the water peak, the −OH peak belonging to the ligands could not be seen in this region (Table 3). The peaks belonging to the carbonyls at 1674 cm^{-1} and 1678 cm^{-1} of the IR spectra of EDTA and 2,3-DHBA, respectively, shifted to 1658 cm^{-1}. This shift supports complex formation.

^{1}H NMR Results. ^{1}H NMR and ^{13}C NMR spectra of the diamagnetic LaAB complex could be taken. The NMR spectra of the EDTA and LaAB complex were taken in D_2O, and also, the ^{1}H NMR spectrum of 2,3-DHBA in DMSO-d_6 was taken. The obtained data are seen in Table 4. According to the ^{1}H NMR spectrum of EDTA, the peaks of CH_2 protons linked to carboxylic acids are observed at 3.70 ppm, and the peaks of CH_2 protons linked to nitrogen are observed at 3.48 ppm. According to the ^{1}H NMR spectrum of the LaAB complex, two peaks were observed at 3.22 ppm and 2.50 ppm. These peaks belong to CH_2 protons linked to carboxylic acids and CH_2 protons linked to nitrogen, respectively. Shifts in peak values are caused by complex formation. In the ^{1}H NMR spectrum of the LaAB complex, three additional peaks are seen at 7.20 ppm, 6.88 ppm, and 6.65 ppm. These peaks show aromatic ring protons of 2,3-DHBA. The fact that the peaks of catecholate protons are not observed shows that complex formation was form in the catecholate mode. In comparison with the peaks of the ^{1}H NMR spectrum of 2,3-DHBA, shifts were observed in peak values. Consequently, it may be said that the obtained complex contains both EDTA and 2,3-DHBA; in other words, the LaAB complex was formed.

Table 4. ^{1}H NMR Spectrum Data of Ligands and Mixed Ligand Complex

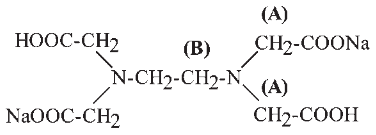
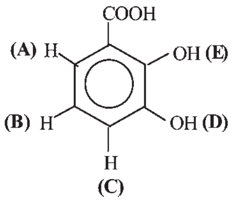
Ligand	Structure Formula with Marked Hydrogen Atoms	Marked Hydrogen	Shifts / (ppm)	
			Ligand alone	LaAB complex
EDTA		A	3.700	3.216
		B	3.482	2.502
2,3-DHBA		A	7.266	7.203
		B	7.033	6.880
		C	6.752	6.630
		D	9.342	-
		E	11.306	-

Table 5. ^{13}C NMR Spectrum Data of Ligands and Mixed Ligand Complex

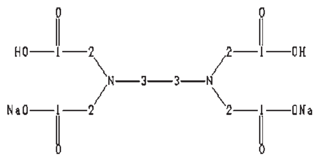
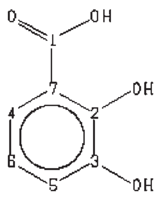
Ligand	Structure Formula with Marked Carbons	Carbon	Shifts / (ppm)	
			Ligand alone	LaAB Complex
EDTA		1	170.525	180.075
		2	57.843	61.702
		3	51.420	54.471
2,3-DHBA		1	172.927	175.544
		2	150.030	148.824
		3	146.330	143.775
		4	121.144	121.640
		5	120.389	119.130
		6	119.023	118.581
		7	113.532	118.375

Table 6. Elemental Analysis Data

	% C	% N	% H	% La	% Na
experimental	28.09	3.84	2.84	20.69	12.2
theoretical	28.18	3.87	2.90	19.21	12.7

^{13}C NMR Results. Three carbon peaks belonging to EDTA and seven carbon peaks belonging to 2,3-DHBA were observed in the obtained ^{13}C NMR spectrum of the LaAB complex. The data obtained from the ^{13}C NMR spectra of EDTA, 2,3-DHBA, and the ternary complex are seen in Table 5. In the ^{13}C NMR spectrum of EDTA taken in D_2O, the carboxylate carbons were observed at 170.53 ppm; $-CH_2$ carbons linked to the carboxylate carbon were observed at 57.84 ppm, and $-CH_2-$ carbons belonging to ethylenediamine were observed at 51.42 ppm. These peaks were observed at 180.08 ppm, 61.70 ppm, and 54.47 ppm, respectively, in the ^{13}C NMR spectrum of the LaAB complex. In the ^{13}C NMR spectrum of 2,3-DHBA taken at DMSO-d_6, the peaks at 172.927 ppm, 150.03 ppm, 146.33 ppm, 121.14 ppm, 120.39 ppm, 119.02 ppm, and 113.53 ppm belong to carboxylate carbon and 2, 3, 4, 5, 6, and 7 numbered carbons in benzene ring, respectively. In the ^{13}C NMR spectrum of the mixed ligand complex of La(III), these carbons were observed at 175.54 ppm, 148.82 ppm, 143.78 ppm, 121.64 ppm, 119.13 ppm, 118.58 ppm, and 118.38 ppm, respectively. Because carbon atoms belonging to both of the ligands were observed in the ^{13}C NMR spectrum of the complex and due to shifts in the peaks, this supports the conclusion that the LaAB mixed ligand complex was formed.

Elemental Analyses. The results of C, N, and H analyses of the LaAB complex are seen in Table 5. According to the data, it is supported that the predicted structure is $LaC_{17}H_{15}N_2O_{12}Na_4 \cdot 3H_2O$ ($M = 724\ g \cdot mol^{-1}$) (Table 6). The sodium amount in the LaAB complex was determined by atomic emission spectrophotometry. As a result of the analyses, the sodium amount was determined as 12.25 %. The theoretical sodium amount, which must exist in the structure predicted for the sample in the same amount, is 12.72 % (Table 6).

Conductivity Results. The conductivity of the LaAB complex was measured. Its molar conductivity was calculated to be 474.67 $\Omega^{-1} \cdot cm^{-1} \cdot mol^{-1}$. This result corresponds to the presence of ∼5 ions.[26] Conductivity measurements in aqueous media yield a consistent result with the predicted structure.

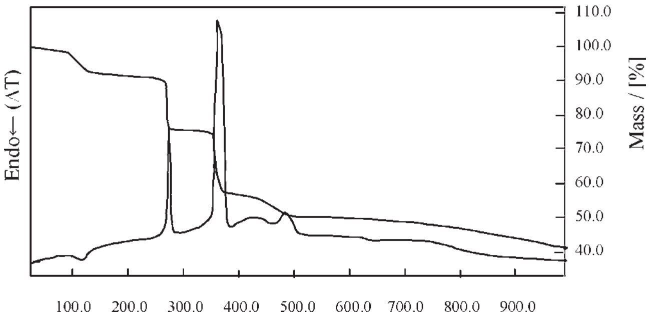


Figure 5. DTA and TG curves of the LaAB complex.

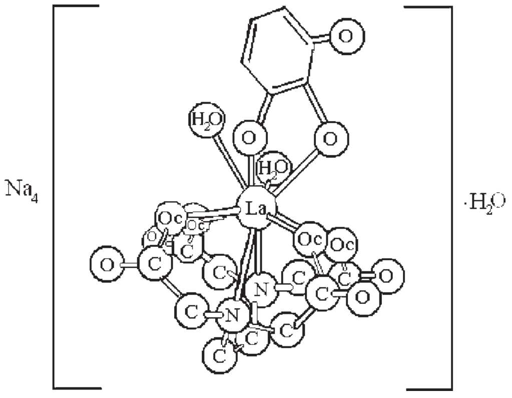


Figure 6. Scaled model of the $Na_4[LaAB(H_2O)_2] \cdot H_2O$ complex.

Thermal Decomposition. The thermal stability and decomposition of the LaAB complex were investigated through thermal analysis (DTA) and thermogravimetric analysis (TG) and under dry air flow at (0 to 1000) °C. The obtained DTA and TG curves are seen in Figure 5. In general, the loss in mass occurred in two steps. The first is the decomposition at 271.8 °C, and the second is decomposition at 360.5 °C. The loss in mass up to 271.8 °C is caused by the loss of water in the structure and was determined as 7.80 % (theoretically 7.46 %). These two values are consistent with each other and correspond to 3 moles of water. The mass left as a result of decomposition at 1000 °C is 42.0 %. It is believed that $La_2O_3 + Na_2O$ would be left as a result of decomposition. Consequently, the theoretical amount left as a result of decomposition is 39.6 %. This value is quite consistent with the empirical result (La_2O_3: mp: 2304 °C, bp: 3620 °C; Na_2O: mp: 1132 °C (dec)).[27]

The percentage by mass of La_2O_3 was determined at 1150 °C through a gravimetric analysis method. La_2O_3 and residual Na_2O were detected in the media at 1150 °C as a result of decomposition of the predicted structure. In other words, most of the Na_2O left the media at 1132 °C.[27] The percentage by mass of the rest was obtained as 24.27 % through the analysis. The theoretical amount of La_2O_3 after decomposition is 22.51 %. It is seen that these two values are close to each other. The La % amount, which was determined by gravimetric analysis, is 20.69 % (Table 6). This is consistent with the theoretical value (19.21 %). These obtained values are indicators for formation of the predicted complex. It is supported that the mixed ligand complex is in the form of $Na_4[LaAB(H_2O)_2]\cdot H_2O$.

CONCLUSION

In the present study, potentiometric equilibrium measurements have been performed at 25 °C and an ionic strength of I = 0.1 M NaCl for the interaction of the polydentate ligand EDTA and 2,3-DHBA with La(III) in a 1:1:1 ratio, and the mixed ligand complex LaAB was synthesized.

The stability constants (log) of the LaA, LaB, and LaAB complexes are 14.60, 12.10, and 19.82, respectively. EDTA and 2,3-DHBA form stable binary complexes with La(III). However, when the 2,3-DHBA binds to the La(III)/EDTA complex as a secondary ligand to form a mixed ligand complex there appear to be steric and electrostatic effects. EDTA is a bulky ligand, and it is more difficult for 2,3-DHBA to bind to a La(III)/EDTA complex than to bind to an La(III) ion. Apart from this, the LaA complex formed by La(III) with EDTA that is shown with formula H_2L^{2-} is negatively loaded. It is difficult for an anionic secondary ligand such as 2,3-DHBA to bind to a negatively loaded LaA complex due to electrostatic effects. Due to these two effects, the stability of the mixed ligand complex is lower than the binary complex.

Lind et al. determined in their study[10] that the coordination number of La(III) in the La(III)/EDTA complex is 10. In this case, the six donor atoms of EDTA and four waters were linked to La(III). 2,3-DHBA was coordinated to La(III) by making a bond in the catecholate mode in the mixed ligand complex, whose formula is $LaC_{17}H_{15}N_2O_{12}Na_4\cdot 3H_2O$. It may be said that two of the three moles of water, which was suggested for the complex, was bound to La(III) as seen in Figure 6 and the other one mole is present as hydrate water, that is, $Na_4[LaAB(H_2O)_2]\cdot H_2O$.

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