



Trade Science Inc.

ISSN : 0974 - 746X

Volume 8 Issue 1

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 8(1), 2013 [20-26]

Potentiometric studies and synthesis of a mixed ligand complex of the Sc (III) ion

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ABSTRACT

The stability constant of a mixed ligand complex of the Scandium ion by using ethylenediaminetetraacetic acid (EDTA, H₂A) as a primary ligand, and 2,3-dihydroxybenzoic acid (2,3-DHBA, H₃B) as a secondary ligand has 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 complex by potentiometry was isolated as solid and the structural characterization have been examined using IR, NMR, elemental analysis, AAS, ICP-OES, differential thermal analysis, thermogravimetric analysis method. © 2013 Trade Science Inc. - INDIA

KEYWORDS

DTA;
2,3-DHBA;
Scandium (III);
Mixed ligand complex.

INTRODUCTION

Scandium is group III element. As the first member of group III, Sc (III) ion with the smallest ion radius ($r = 0.075$ nm), which is intermediate between the radii of the Al (III) ion (0.054 nm) with a coordination number of six and the Y (III) ion (0.090 nm) with a coordination number of eight^[1,2]. It has been considered for a long period that the Sc (III) ion coordinates six water molecules, by analogy with the structure of a large number of studied crystal hydrates with oxygen-containing ligands^[3]. However, publications^[4,5] showed that the coordination number of the Sc (III) ion varies over a broad range from three to nine in complexes with oxygen donor ligands. Scandium ion, Sc (III), has the electron configuration of inert gases (d^0); this makes its interactions clearly electrostatic. The metal ion Sc (III) is hard Lewis acid and it form complexes preferentially

with hard Lewis base such as O-containing ligands. For example, the stability constants for 1:1 complexes of Sc (III) and EDTA are 10^{23} ^[6].

Ethylenediaminetetraacetic acid (EDTA, H₂A) is a polyamino carboxylic acid and It has been previously known that EDTA have 6 coordination numbers (2 nitrogens and 4 carboxylates) with alkaline earth and diamagnetic lanthanide cations (La (III), Lu (III) and Y (III))^[7,8]. Smaller ligands form ternary complexes with M (EDTA).

Researcher were synthesized NH₄[Sc(EDTA)(H₂O)₂].3H₂O^[9]. The Sc (III) has coordination number eight, which includes four O and two N atoms of the EDTA and two O atoms of coordinated water. These eight atoms form a distorted square antiprism around the Sc (III)^[9]. Turkel et al. investigated the complexes of S (III) with 2,3-DHBA at 25°C and under 0.1 M KNO₃ ionic medium through potentiometric methods

and they determined the stability constants of ScB and ScB (H₂B) complexes as 21.36 and 23.03, respectively^[10]. Besides simple coordination species like binary systems consisting of single type metal ion and single type ligand in organisms and ecosystems, number of the chemical equilibria in which including coordination species containing more than one metal ion and/or more than one ligand type take place is quite high. Consequently, mixed ligand studies have become more important recently to describe these systems and to contribute to application of it for various purposes^[11]. Although there are studies on binary systems produced by ethylenediaminetetraacetic acid and 2,3-dihydroxybenzoic acid with the Sc (III) ions in the literature, there is no study on the mixed complexes with these two ligands. Therefore, in this study, the stability constants of mixed ligand complexes that these ligands form Sc (III) was investigated in aqueous solution and the mixed ligand complex was isolated in the solid state and characterized.

EXPERIMENTAL

Chemicals

All chemicals were of analytical grade and used without further purification. Scandium oxide (Sc₂O₃, 99%) and 2,3-dihydroxybenzoic acid (2,3-DHBA, 97%) were purchased from Aldrich, and the disodium salt of ethylenediaminetetraacetic acid (Na₂EDTA, 99%) was purchased from Merck. The purities of the ligands were checked by potentiometry^[12]. A stock solution of Sc (III) was prepared by dissolving the proper amount of Scandium oxide (Sigma 99.9%) in a small amount 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 Sc (III) was standardized complexometrically by EDTA titration using the method of Schwarzenbach^[13].

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 kept 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⁺]^[14]. This is because the EMF values (E) depend on [H⁺] according to $E = E^{\circ} + \text{slog} [H^{+}] + J_{H}[H^{+}] + J_{OH}[OH^{-}]$, 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^[15] and a total volume of 50 mL was used for each titration.

Calculation

To calculate the stability constants of binary and mixed ligand complexes, the data for the potentiometric titrations was treated using the microcomputer program BEST^[16]. This comprises the best reaction model and applies the criterion for which species are present in equilibria and 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^[16]; thus, the species existing in the Sc (III):EDTA:2,3-DHBA system are available.

TABLE 1 : Protonation constants (log K ± σ)^y of EDTA and 2,3-DHBA at ionic strength I = 0.1 M NaCl and 25 °C.

Ligand	log K ₁	log K ₂	log K ₃
EDTA	9.48 ± 0.05	6.06 ± 0.04	-
	10.17 ¹⁸	6.11 ¹⁸	-
	9.42 ± 0.05 ¹⁹	6.22 ± 0.05 ¹⁹	-
2,3-DHBA	12.20 ± 0.40	10.00 ± 0.20	2.72 ± 0.21
	>14 ¹⁸	9.81 ²⁰	3.32 ²⁰
		9.91 ²¹	2.74 ²¹

x : standard deviation; y : ± 95 % confidence interval

Potentiometric titrations

Potentiometric titrations were carried out using

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three different metal concentrations [$(2.0 \times 10^{-3}, 3.0 \times 10^{-3}$ and $4.0 \times 10^{-3})$ M]. The experimental procedure involved the potentiometric titrations of the following solutions:

- 5 mL 0.1 M HCl + 5 mL 1 M NaCl (for cell calibration).
- 5 mL 0.1 M HCl + 0.1 mmol ligand A or B + 5 mL 1 M NaCl (for the determination of the protonation constants of ligands).
- Solution b + 10 mL 0.01 M Sc (III) (for the determination of the stability constants of ScB or ScA complexes).
- Solution a + 0.1 mmol ligand A + 0.1 mmol ligand B + 10 mL 0.01 M (0.1 mmol) Sc (III) (for the determination of the stability constants of the ScBA 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 4.00-11.00 as a function of millimoles of the standard 0.1 M base.

Spectroscopic study

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

Synthesis of the mixed ligand complex

1 mmol Sc_2O_3 is dissolved with concentrated HCl to prepare a Sc (III) solution. The EDTA and 2,3-DHBA ligands are added to the prepared Sc (III) solution in equal millimolar concentrations. The pH of the solution is adjusted to 9.7 with NaOH and mixed for a day. The obtained solution is left to crystallize. Small crystals are obtained from the complex solutions. After they are filtered and dried, however, they turn into a 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 the 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 278.8 °C (decomposition) and the efficiency is 53% (0.47g).

RESULTS AND DISCUSSION

Proton-ligand systems

The protonation constants of EDTA (H_2A^{2-}) and 2,3-DHBA (H_3B) were determined again by the potentiometric method at 25 °C and in a 0.1M ionic medium (NaCl)^[17]. The agreement between the present data is very good with the previous results^[10,18-21] (TABLE 1).

Metal-ligand binary systems

The complexation behavior of EDTA and 2,3-DHBA toward Sc (III) ions in aqueous solution was studied by potentiometry. A representative pH-metric titration curve of this binary system is shown in Figure 1, curve IV and V. Analysis of the complexes and ligands curve indicates that the addition of metal ion to the free ligand solutions shifts the buffer region of the ligand to lower pH. This result indicates that complex formation reactions proceed by release of protons from such ligands. It is possible to show the formation reaction and the stability constant equation of the ScA and ScB binary complex with eq 1 and 2:

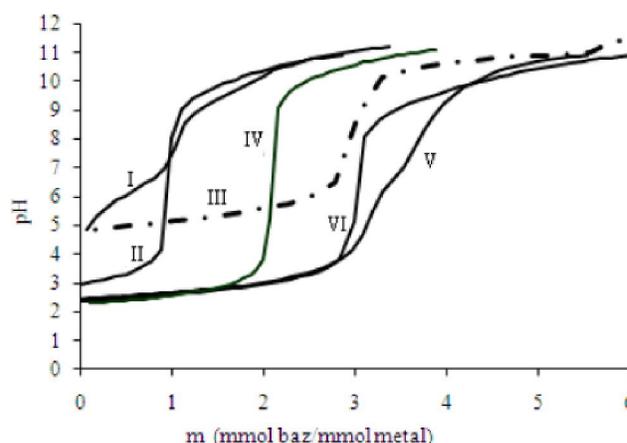
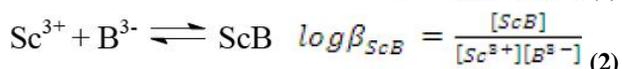
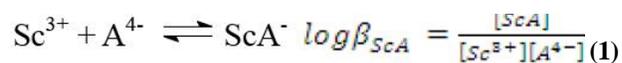


Figure 1 : Potentiometric titrations curves of Sc(III):EDTA:2,3-DHBA system at 25 °C and I = 0.1 M NaCl; a) EDTA alone; b) 2,3-DHBA alone; c) Sc(III):EDTA (1:1); d) Sc(III):2,3-DHBA (1:1) e) Sc(III):EDTA:2,3-DHBA (1:1:1)

The stability constant for the ScA and ScB complexes were redetermined by the BEST computer program according to the potentiometric data in this stud-

ies ; the agreement was very good with previous results^[18,22-25] (TABLE 2). The distribution curves were drawn for the Sc:EDTA and Sc (III):2,3-DHBA systems by the SPE program (Figure 2a and 2b). According to the distribution curve drawn for the Sc (III):EDTA system (Figure 2a), the ScA type complexes are produced at approximately 100% of the Sc (III) at pH 2. The ScB complex is present at approximately 98% between pH 4.0 and 7.0 (Figure 2b).

TABLE 2 : Stability constants ($\log \beta(K) \pm \sigma^y$) of binary and mixed ligand complexes of Sc(III) at ionic strength $I = 0.1$ M NaCl and 25 °C.

$\log \beta_{ScA}^2$	$\log \beta_{ScB}^2$	$\log K_h$	$\log K_{ScA}^{ScA}$	$\log \beta_{ScAB}$
23.1±0.02	20.81±0.03	12.31±0.11	5.49±0.01	29.59±0.01
23.1 ²²				
23.0 ²³				
25.05 ²⁴	21,36 ¹⁰	-	-	-
21.0 ²⁵				

x : standard deviation; y : ± 95 % confidence interval;

Metal-ligand ternary systems

Potentiometric titrations of the (1:1:1) mole ratio Sc (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 Sc (III):EDTA:2,3-DHBA system (Figure 1, curve II and VI), a decrease in pH is seen. The decrease in pH indicates that a ScAB complex has been formed. The potentiometric titration curve of Sc (III) ion is given in Figure 1, curve III. Continuous deviation is observed at the pH values between $m=0.0$ and 3.0 A wide buffer zone occurs due to hydrolysis of $[Sc(H_2O)_n]^{3+}$ ion. It can be said that the $[Sc(H_2O)_n]^{3+}$ ion is hydrolyzed after pH=5. When potentiometric titration curves of the Sc (III) and ScAB complex were compared, the difference was seen.

These results show that the proton titrated is due to complex formation. The formation reactions and overall stability constant of the ScAB complex in the Sc (III):EDTA:2,3-DHBA system are shown by eq 3:



The stability constants of the ScAB complex are listed in TABLE 2. According to the distribution curve of the Sc (III):EDTA:2,3-DHBA system (Figure 2c), the

ScAB complex began to form around pH~8.5 and is present at approximately 90% after pH 11.

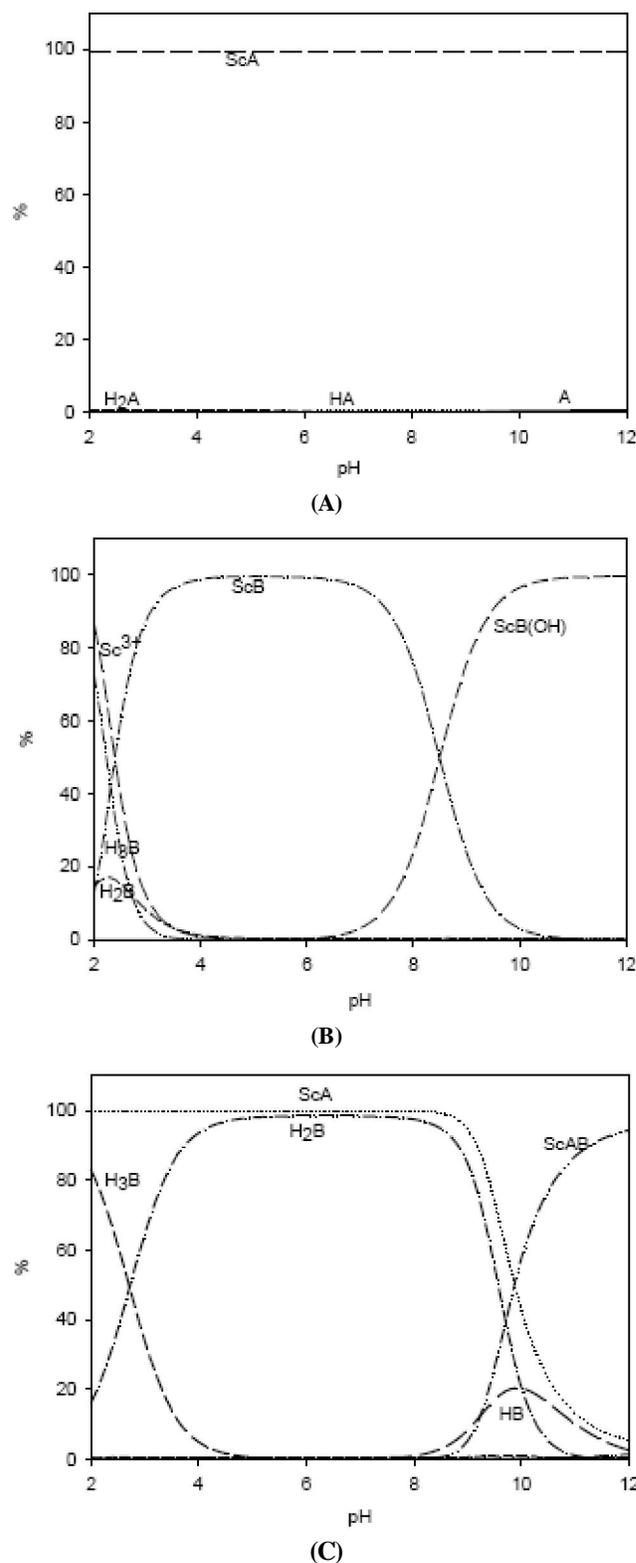


Figure 2 : Distribution diagrams of Sc(III):EDTA:2,3-DHBA System a) Sc(III):EDTA (1:1), b) Sc(III):2,3-DHBA (1:1), c) Sc(III): EDTA:2,3-DHBA (1:1:1).

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Spectroscopic results

The recorded electronic spectra of the 2,3-DHBA at different pH = 3.5-10.5 are shown in Figure 3a. The whole spectra are presented in two sets according to the ligand peak at 306 nm (pH = 3.80), 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 happens due to the conversion of the COOH group into a COO⁻ ion, whereas the red shift is assigned (pH= 10.3, $\lambda_{\text{max}}=317.4$ nm) to the deprotonation of the hydroxyl group^[26].

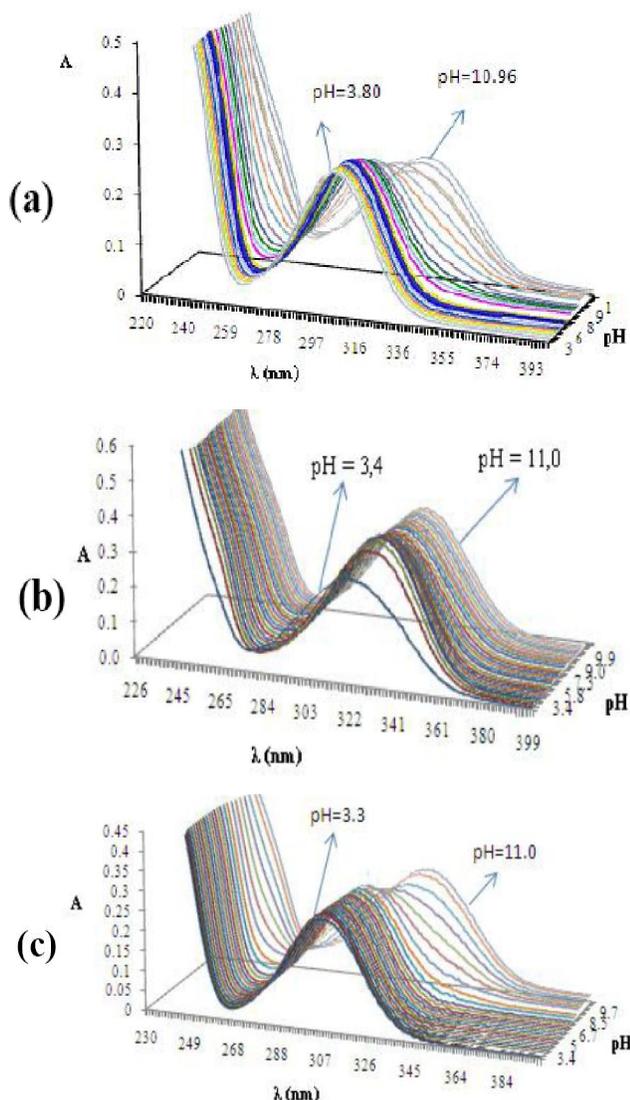


Figure 3 : Spectra of Sc(III):EDTA:2,3-DHBA System at Different pH a) 2,3-DHBA alone, b) Sc(III):2,3-DHBA (1:1) (c) Sc(III):EDTA:2,3-DHBA (1:1:1).

The spectra of the solutions containing Sc (III):2,3-DHBA and Sc (III):EDTA:2,3-DHBA are taken be-

tween pH 3.30 and 11.0 within the 190-400 nm wavelength interval (Figure 3b and 4c). The wavelength peak shifts to red in the spectra taken after pH 4.3 for ScB and pH 9.5 for ScAB. This shifting to red in the spectra indicates that the ligand is bound by the phenolic oxygen to form the binary and mixed ligand complex.

Identification of structure of mixed ligand complex

IR (KBr) ν

For EDTA, (3381.5, 3027.0, 1674 cm⁻¹)

For 2,3-DHBA, (3368.4, 3047.3, 1678.2 cm⁻¹).

For Mixed ligand complexes, (3000-3500, 3043.8, 2962.1, 1638.1, 1613.6 cm⁻¹).

Coordination and/or crystal waters exist in the structure of the obtained complex. Because the 3000-3500 cm⁻¹ region is overlapped by the water peak, the -OH peak belonging to the ligands cannot be seen in this region. The peaks belonging to the carbonyls at 1674 cm⁻¹ and 1678.2 cm⁻¹ of the IR spectra of EDTA and 2,3-DHBA, respectively, shifted to 1638.1 cm⁻¹ and 1613.60 cm⁻¹. This shift in the peak at 3043.8 shows that the presence of aromatic C-H bindings in the structure supports complex formation.

¹H-NMR results

For EDTA (D₂O, 300MHz) δ : 3.70 (s,8H), 3.48 (s,4H)

For 2,3-DHBA (DMSO, 300MHz); 6.75 (s, 1H), 7.03 (s, 1H), 7.27 (s, 1H), 9.34 (s, 1H), 11.31 (s, 1H),

For Mixed ligand complexes (DMSO, 300MHz); 3.35- 3.11 (dd, J=10.4, J=5,6 Hz, 8H), 2.64 (s, 1H), 7.18 (s, 1H), 6.85 (s, 1H), 6.64 (t, J=0,8 Hz, 1H), 8.36 (s, OH),

According to the ¹H-NMR spectrum of EDTA, the peaks of acetate protons are observed at 3.70 ppm and the peaks of ethylene protons are observed at 3.48 ppm. According to the ¹H-NMR spectrum of the ScAB complex, the quartet peaks for acetate protons are observed. The single peak for ethylene protons is observed at 2.64 ppm. Shifts in peak values are caused by complex formation. In the ¹H-NMR spectrum of the ScAB complex, two singlet and one triplet peaks are seen. These peaks show aromatic ring protons of 2,3-DHBA. The singlet peak belonging to OH protons in the meta- position to the carboxylate of 2,3-DHBA was observed at 8.36 ppm. Also, the peak belonging to the

hydrogen bond between OH protons in the ortho position with the carboxylate oxygen is observed at 16.60 ppm. The $^1\text{H-NMR}$ spectrum of the ScAB mixed ligand complex shows that the binding between Sc (III) and 2,3-DHBA is the carboxylate type. In comparison with the peaks of the $^1\text{H-NMR}$ spectrum of 2,3-DHBA, shifts are observed at the peak values. Consequently, it may be said that the complex obtained contains both EDTA and 2,3-DHBA; in other words, the ScAB complex formed.

$^{13}\text{C-NMR}$ results

Three carbon peaks belonging to EDTA and seven carbon peaks belonging to 2,3-DHBA were observed in the $^{13}\text{C-NMR}$ spectrum obtained of for the ScAB complex. The data obtained from the $^{13}\text{C-NMR}$ spectra of EDTA, 2,3DHBA, and the ternary complex is shown in TABLE 3. In the $^{13}\text{C-NMR}$ spectrum of EDTA taken in D_2O , the carboxylate carbons were observed at 170.53 ppm, $-\text{CH}_2$ carbons linked to the carboxylate carbon were observed at 57.84 ppm and $-\text{CH}_2$ carbons belonging to ethylenediamine were observed at 51.42 ppm. These peaks were observed at 180.10 ppm, 62.62 ppm, and 57.56 ppm, respectively, in the $^{13}\text{C-NMR}$ spectrum of the ScAB complex. In the $^{13}\text{C-NMR}$ spectrum of 2,3-DHBA taken at DMSO-d_6 , the peaks at 172.93 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 the 2, 3, 4, 5, 6, and 7 numbered carbons in the benzene ring, respectively. In the $^{13}\text{C-NMR}$ spectrum of the mixed ligand complex of Sc (III), these carbons were observed at 175.61 ppm, 151.72 ppm, 144.00 ppm, 121.02 ppm, 119.25 ppm, 118.66 ppm, and 118.43 ppm, respectively. The fact that carbon atoms belonging to both of the ligands were observed in the $^{13}\text{C-NMR}$ spectrum of the complex and due to shifts in the peaks supports the conclusion that the ScAB mixed ligand complex was formed.

Elemental analyses

The results of the C, N, and H analyses of the ScAB complex are shown in TABLE 4. The data indicates that the predicted structure is $\text{Na}_2[\text{Sc}(\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}_8)(\text{C}_7\text{H}_5\text{O}_4)].3\text{H}_2\text{O}$ (TABLE 4). The amounts of sodium and Scandium in the ScAB complex were determined by atomic absorption spectrom-

eter (AAS) and inductively coupled plasma optical emission spectrometry (ICP-OES), respectively (TABLE 4).

TABLE 3 : $^{13}\text{C-NMR}$ spectrum data of ligands and mixed ligand complex

$\log \beta_{\text{ScA}}$	$\log \beta_{\text{ScB}}$	$\log K_h$	$\log K_{\text{ScAB}}^{\text{ScA}}$	$\log \beta_{\text{ScAB}}$
23.1±0.02	20.81±0.03	12.31±0.11	5.49±0.01	29.59±0.01
23.1 ²²				
23.0 ²³	21,36 ¹⁰	-	-	-
25.05 ²⁴				
21.0 ²⁵				

x : standard deviation; y : ± 95 % confidence interval

TABLE 4 : Elemental analysis data

	%C	%N	%H	%Sc	%Na
Experimental	34.11	4.95	3.82	7.15	8.28
Theoretical	34.81	4.78	3.92	7.68	7.85

Thermal decomposition

The thermal stability and decomposition of the ScAB complex were investigated through thermal analysis (DTA and thermogravimetric analysis (TG) and under dry air flow at (25 to 1000) °C. The DTA and TG curves obtained are shown in Figure 4. In general, the loss in mass occurred in three steps. The first was decomposition at 69.6 °C, the second was decomposition at 278.8 °C, the third was decomposition at 358.4 °C and the fourth was decomposition at 487.7 °C. The loss in mass up to 69.6 °C is caused by the loss of water in the structure and was determined to be 8.6% (theoretically 9.2%). 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 21.20%. It is believed that $\text{Sc}_2\text{O}_3 + \text{Na}_2\text{O}$ will be left as a result of decomposition. Consequently, the theoretical amount left as a result of decomposition is 22.35%. This value is quite consistent with the empirical results (Sc_2O_3 : mp: 2484 °C, Na_2O : mp: 1132 °C (dec)^[27].

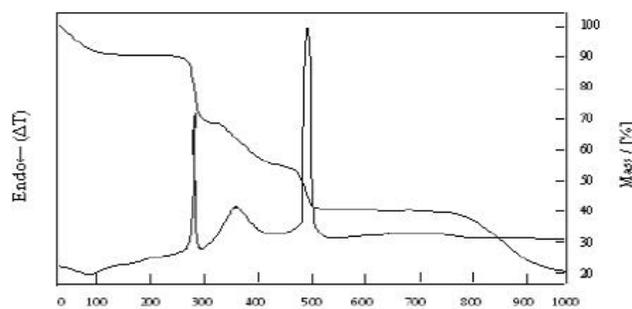


Figure 4 : DTA and TG curves of the ScAB complex.

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CONCLUSIONS

The stability constants of the ScA ($\log \beta_{ScA}^{Sc}$), ScB ($\log \beta_{ScB}^{Sc}$), and ScAB ($\log \beta_{ScAB}^{ScA}$) complexes are 23.1, 20.81 and 5.49, respectively. EDTA and 2,3-DHBA form stable binary complexes with Sc (III). However, when the 2,3-DHBA binds to the Sc (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 Sc (III):EDTA complex than to bind to a Sc (III) ion. Apart from this, the ScA complex formed by Sc (III) with EDTA that is shown with formula H_2A^{2-} is negatively loaded. It is difficult for an anionic secondary ligand such as 2,3-DHBA to bind to a negatively loaded ScA complex due to electrostatic effects. Due to these two effects, the stability of the mixed ligand complex is lower than the binary complex.

Zang et al. determined in their study^[9] that the coordination number of Sc (III) in the Sc (III):EDTA complex is nine. In this case, the six donor atoms of EDTA and two waters were linked to Sc (III). 2,3-DHBA was coordinated to Sc (III) by creating a bond in the carboxylate type in the mixed ligand complex, whose formula is $Na_2[ScAB].3H_2O$. It may be said that the three moles of water is present as hydrate water, i.e.

ACKNOWLEDGEMENT

We thank the Research Foundation of Uludag University (Project Number, KUAP (F)-2012/63) and Tubitak (Project Number, 110T535) for their financial support for the research projects.

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