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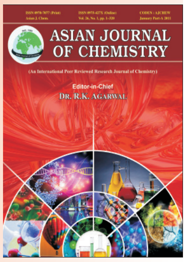

Synthesis and Determination of the Stability Constant of Mixed Ligand Complex of Y(III)

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In this study, the stability constants of a mixed ligand complex of the yttrium ion by using ethylenediaminetetraacetic acid (EDTA, H_2A) as a primary ligand and 2,3-dihydroxy benzoic acid (2,3-DHBA, H_3B) 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 ºC in a 0.1 M NaCl ionic medium. In addition, the identified complex by potentiometry was isolated as solids and the structural characteristics have been examined using IR, NMR, elemental analysis, AAS, ICP-OES, differential thermal analysis, thermogravimetric analysis and the conductivity method.

Keywords: 2,3-Dihydroxy benzoic acid, Yttrium, EDTA, Mixed ligand complex, Stability constant.

INTRODUCTION

Yttrium is a group III element. Yttrium always found in nature with lanthanides and its chemical properties are very similar to the Ln(III) ions; its ionic radius is 1.04 Å[1]. The most common coordination numbers of yttrium(III) are eight and nine[2-8]. The bonds between III group elements and more electronegative partners are essentially ionic. The metal ions M(III) are hard Lewis acids and they form complexes preferentially with hard Lewis bases such as *O*-containing ligands. For example, the stability constants for 1:1 complexes of M(III) and EDTA are 10^{23} (Sc) and 10^{18} (Y)[9]. Aminocarboxylates such as EDTA form multidentate complexes with lanthanide cations (La^{3+}, Lu^{3+} and Y^{3+}), in which six coordination sites of the metal cations are occupied by the EDTA ligand (2 nitrogens and 4 carboxylates) with two or three waters of hydration remaining attached to give a net coordination number ten[10]. Smaller ligands form ternary complexes with M(EDTA). Researchers have synthesized $NH_4[Y(EDTA)(H_2O)_3]\cdot5H_2O$[3] and $Na[Y(EDTA)(H_2O)_3]\cdot5H_2O$[7]. The structural determination shows that the Y(III) ion is coordinated by four O and two N atoms of ethylenediaminetetraacetate (EDTA) ligand by water molecules. All of the four carboxylate groups are monodentates[3,7]. Baisden *et al.*[11] investigated the proton resonance spectra for a complex of Y(III) with EDTA in aqueous solution to learn more about the bonding and structural characteristics of these complexes. In the spectra of Y(EDTA) complexes, quartet peaks for the acetate protons and a singlet peak for the ethylene protons have been observed.

Aydin and Ozer[12] investigated the complexes of Y(III) with 2,3-DHBA at 25 ºC and under 0.1 M $NaClO_4$ ionic medium through potentiometric methods and determined the stability constants of YB and $YB(HB)^{2-}$ complexes to be 16.09 and 20.71, respectively. Kula *et al.*[13] described the complex of Y(III) with 2,3-DHBA and its solubility in water, IR and X-ray spectra and the thermal decomposition in the air atmosphere of the YB complex have been investigated. The YB complex was obtained as tetrahydrates, with a molar ratio of a metal-to-organic ligand of 1:3 and a general formula of $Y[C_6H_3(OH)_2COO]_3.4H_2O$.

Mixed ligand studies have become more important recently to describe systems which is organisms and ecosystems and to contribute to its application of it for various purposes[14].

Therefore, in this study, the stability constants of mixed ligand complexes that is form of Y(III) with EDTA and 2,3-DHBA ligands was investigated in aqueous solution and the mixed ligand complex was isolated in the solid state and characterized.

EXPERIMENTAL

All chemicals (yttrium oxide, 99 %, 2,3-dihydroxy benzoic acid, 97 %, disodium salt of ethylenediaminetetraacetic acid, 99 %) were of analytical grade and used without further purification. The purities of the ligands were checked by potentiometry[15]. A stock solution of Y(III) was prepared by dissolving the proper amount of yttrium 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 of Y(III) was checked by potentiometric titration. The stock solution of Y(III) was standardized complexometrically by EDTA titration using the method of Schwarzenbach and Flaschka[16].

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 ± 0.1 ºC by circulating water from an external thermostat (VWR, precision ± 0.1 ºC). The pH-meter was calibrated daily using standard buffer solutions (Merck) with pH values of 4.01, 6.96 and 8.96 at 25 ºC. 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, as previously[17]. The ionic strength of the solutions were adjusted to 0.1 M by NaCl[18] and a total volume of 50 mL was used for each titration. Potentiometric titrations were carried out using three different metal concentrations [$(2 \times 10^{-3}$, 3×10^{-3} and $4 \times 10^{-3})$ M]. The experimental procedure involved the potentiometric titrations of the following solutions:

(a) 5 mL 0.1 M HCl + 5 mL 1 M NaCl (for cell calibration).

(b) 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).

(c) Solution b + 10 mL 0.01 M Y(III) (for the determination of the stability constants of YB or YA complexes).

(d) Solution a + 0.1 mmol ligand A + 0.1 mmol ligand B + 10 mL 0.01 M (0.1 mmol) Y(III) (for the determination of the stability constants of the YBA mixed ligand complex).

To calculate the stability constants of binary and mixed ligand complexes, the data for the potentiometric titrations was treated using the microcomputer program BEST[19], as previously described[18,20]. The species distribution diagrams were obtained using the SPE program[19].

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

IR absorpsition spectra of the ligands and the mixed ligand complex were recorded as KBr pellets on a Thermo FT-IR spectrophotometer (Nicolet 6700). By a standart procedure.

NMR experiments were performed on a Varian Mercury Plus 400 MHz spectrometer. The ^{1}H NMR and ^{13}C NMR spectra of the diamagnetic YAB complex could be taken. The NMR spectra of the EDTA is taken in D_2O and the NMR spectrum of 2,3-DHBA is taken in DMSO-d_6 and the YAB complex are taken both in DMSO-d_6 and in D_2O.

Thermogravimetric (TG) and differential thermogravimetric (DTG) curves were obtained using a SII Exstar TG/DTA 6200 analyser in the range 25-100 °C in platinum crucibles under nitrogen at a heating rate of 10 °C min^{-1} using alumina as reference.

The elemental analyses were performed on a Costech CHNS analyzer.

Sodium analyses were perfomed on a Varian spectra 220-FS atomic absorption spectrometer. Yttrium metal analyses were performed on a Perkin Elmer Optima 2100 DV inductively coupled plasma optical emission spectrometer (ICP-OES). Conductimetric measurements were performed on a WTW inoLab Cond 730 Conductimeter.

RESULTS AND DISCUSSION

Typical titration curves of EDTA (H_2A^{2-}) and 2,3-DHBA (H_3B) solutions in either the absence or pre-absence of Y(III) metal ion at 25 ºC and in a 0.1 M NaCl are shown in Fig. 1, where *m* is moles of base added per mole of ligand. Analysis of the complexes and ligands curve indicates that the addition of Y(III) 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. The protonation constants for EDTA and 2,3-DHBA and stability constant for the YA and YB complexes were redetermined by the BEST computer program according to the potentiometric data in this studies; the agreement was very good with previous results[12,21-27] (Table-1 and 2).

TABLE-1
PROTONATION CONSTANTS (log K ± $\sigma^x)^y$ OF EDTA AND 2,3-DHBA AT IONIC STRENGTH I = 0.1 M NaCl AND 25 ºC

Ligand	log K_1	log K_2	log K_3
EDTA	9.48 ± 0.05	6.06 ± 0.04	-
	10.17[20]	6.11[20]	-
	9.42 ± 0.05[24]	6.22 ± 0.05[24]	
2,3-DHBA	12.20 ± 0.40[20]	10.00 ± 0.20[20]	2.72 ± 0.21[20]
	> 14[21]	9.81[22]	3.32[23]
		9.91[23]	2.74[23]

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

TABLE-2
STABILITY CONSTANTS (log β(K) ± $\sigma^x)^y$ OF BINARY AND MIXED LIGAND COMPLEXES OF Y(III) AT IONIC STRENGTH I = 0.1 M NaCl AND 25 ºC

log β_{YA}	log β_{YB}	log β_{YH2B}	log K^{YA}_{YAB}	log β_{YAB}
18.01 ± 0.02	15.43 ± 0.27	25.22 ± 0.06	4.95 ± 0.03	22.72 ± 0.48
18.08[21]	16,09 ± 0,04[11]	-	-	-
17.38[23]				
18.5[24]				
18.09[25]				

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

Metal-ligand ternary sistems: Potentiometric titrations of the (1:1:1) mole ratio Y(III):EDTA:2,3-DHBA system were performed in I = 0.1 M NaCl ionic medium and at 25 ºC. In the mixed ligand system, one inflection point was observed at m = 3. In comparison with the titration curves of 2,3-DHBA for the Y(III):EDTA:2,3-DHBA system (Fig. 1, curve **b** and f), a decrease in pH is seen. The decrease in pH indicates that a YAB complex has been formed. The potantiometric titration curve of Y(III) ion is given in Fig. 1, curve **c**. Continuous deviation is observed at the pH values between m = 0.5 and 2.5. A wide buffer zone occurs due to hydrolysis of $[Y(H_2O)_n]^{3+}$ ion. It can be said that the $[Y(H_2O)_n]^{3+}$ ion is hydrolyzed after pH = 7. When potantiometric titration curves of the Y(III) and YAB 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 YAB complex in the Y(III):EDTA:2,3-DHBA system are shown by eqn. 1:

$$Y^{3+} + A^{4-} + B^{3-} \rightleftharpoons YAB^{4-}$$

$$\log\beta^{Y}_{YBA} = \frac{[YBA^{4-}]}{[Y^{3+}][A^{3-}][B^{4-}]} \qquad (1)$$

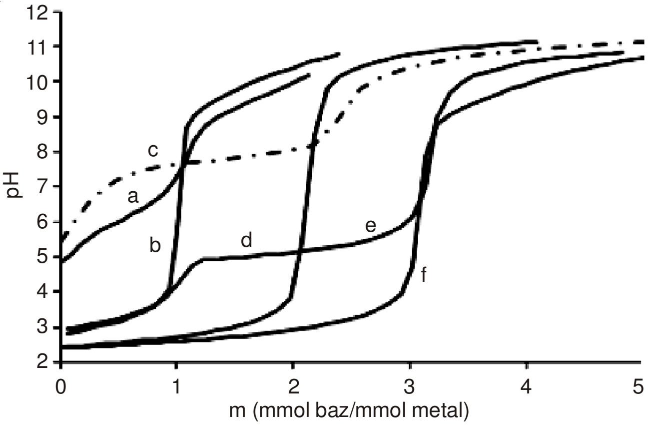

Fig. 1. Potentiometric titrations curves of Y(III):EDTA:2,3-DHBA System at 25 °C and I = 0.1 M NaCl; a) EDTA alone; b) 2,3-DHBA alone; c) Y(III):EDTA (1:1); d) Y(III):2,3-DHBA (1:1) e) Y(III):EDTA:2,3-DHBA (1:1:1)

The stability constants of the YAB complex are listed in Table-2. According to the distribution curve of the Y(III): EDTA:2,3-DHBA system (Fig. 2c), the YAB complex began to form around pH-9 and is present at approximately 80 % after pH 11.

Spectroscopic results: The electronic spectra of the solutions containing 2,3-DHBA, Y(III):2,3-DHBA and Y(III): EDTA:2,3-DHBA at different pH = 3.5-10.5 are taken (Fig. 3a, 3b, 3c). The first blue shift that the electronic spectra of the 2,3-DHBA happens due to the conversion of the COOH group into a COO- ion, whereas the red shift is assigned (pH = 10.3, λ_{max} = 317.4 nm) to the deprotonation of the hydroxyl group[28].

The wavelength peak shifts to red in the spectra taken after pH 5 for YB and pH 9.8 for YAB. This shifting to red in the spectra indicates that the ligand is bound by the catecholic oxygen to form the binary and carboxylate oxygen to from mixed ligand complex.

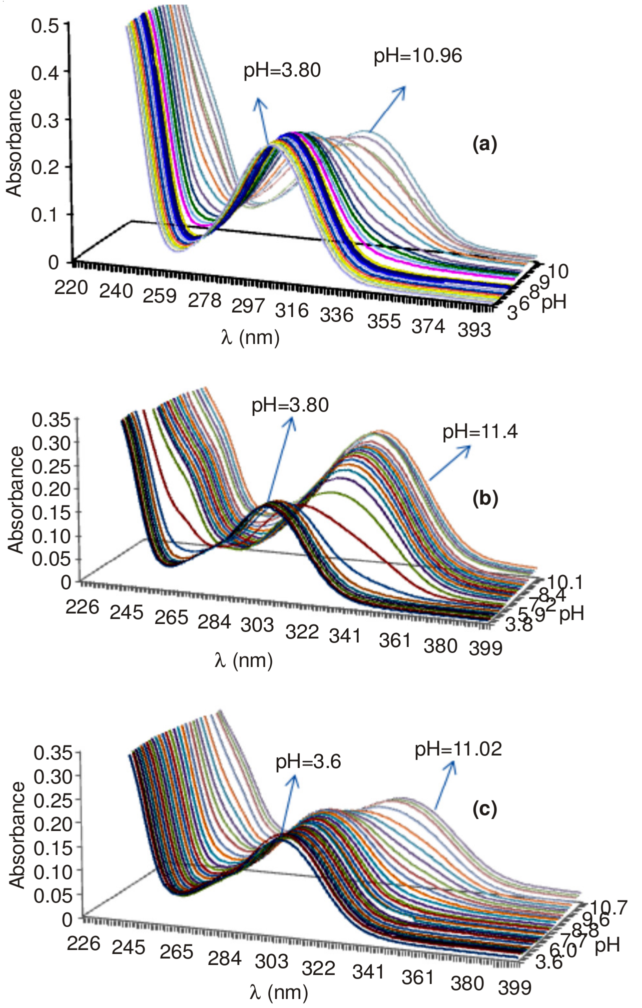

Fig. 3. Spectra of Y(III):EDTA:2,3-DHBA system at different pH a) 2,3-DHBA alone, b) Y(III):2,3-DHBA (1:1) (c) Y(III):EDTA:2,3-DHBA (1:1:1)

Characterization mixed ligand complex: IR (ν, cm^{-1}): 3500-3000 cm^{-1} ν(H_2O), 1674 cm^{-1} and 1678 cm^{-1} ν(C=O), 3043.8 cm^{-1} ν(C-H$_{(arom)}$)), 2933.50 ν(C-H$_{(aliph)}$))

^{1}H NMR (δ, ppm): For EDTA; 3.70 (s,CH_2), 3.48

For 2,3-DHBA; 7.27 (s, C_6H_3), 7.03 (s, C_6H_3), 6.75 (s, C_6H_3), 9.34 (s, OH), 11.31 (s, OH),

For Mixed ligand complexes; 3.35-3.11 (q, CH_2), 2.64 (s, CH_2), 7.19 (s, C_6H_3), 6.85 (s, C_6H_3), 6.63 (s, C_6H_3), 8.33 (s, OH),

^{13}C NMR (δ, ppm): For EDTA; 170.53 (C1), 57.84 (C2), 51.42 (C3),

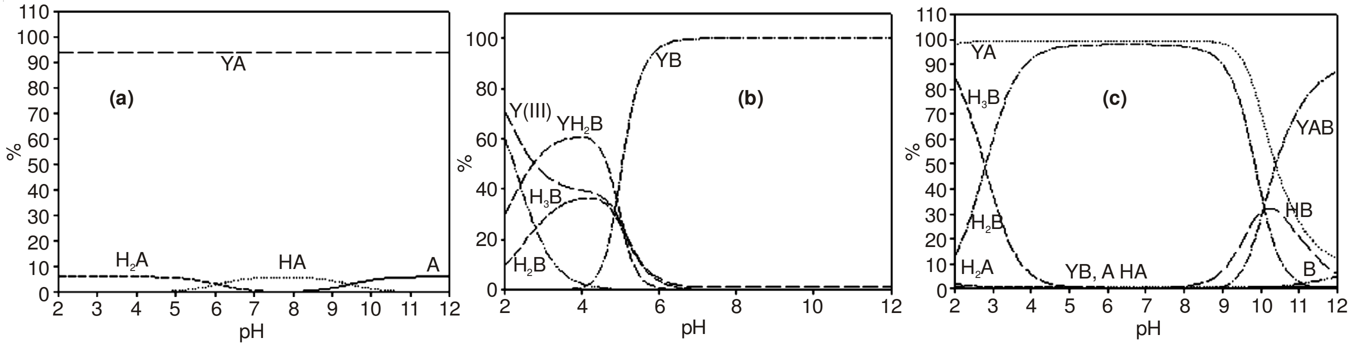

Fig. 2. Distribution diagrams of Y(III):EDTA:2,3-DHBA system a) Y(III):EDTA (1:1), b) Y(III):2,3-DHBA (1:1), c) Y(III): EDTA:2,3-DHBA (1:1:1)

For 2,3-DHBA; 172.93 (C4), 150.03 (C5), 146.33 (C6), 121.14 (C7), 120. 39 (C8), 119.02 (C9), 113.53 (C10)

For Mixed ligand complexes; 179.95 (C1), 62.65 (C2), 57.52 (C3), 175.62 (C4), 151.57 (C5), 144.23 (C6), 121.41 (C7), 119.23 (C8), 118.54 (C9), 118.38 (C10) (Fig. 4).

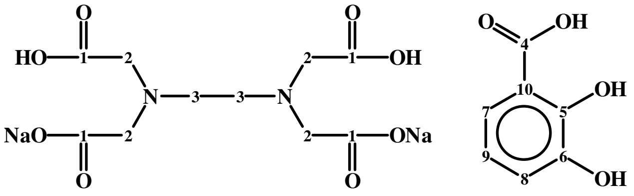

Fig. 4. Structure formula with marked carbons for ligands

Elemental analyses: For $Na_2[Y(C_{10}H_{15}N_2O_8)(C_7H_5O_4)(H_2O)].5H_2O$. Anal. calcd. (%): C, 29.82; N, 4.09; H,4.09; Y, 14.18; Na, 6.73. Found, (%): C, 29.70; N, 4.50; H,3.95; Y, 13.80; Na, 7.06

Conductumetry results: The conductivity of the YAB complex was measured. Its molar conductivity was calculated to be 263.68 ohm^{-1} cm^{-1} mol^{-1}. This result corresponds to the presence of ~3 ions[29]. Conductivity measurements in aqueous media yielded a result consistent with the predicted structure.

Thermal decomposition: The thermal stability and decomposition of the YAB complex were investigated through thermal analysis (DTA and thermogravimetric analysis (TG) and under dry air flow at (25 to 1000) ºC. Fig. 5 shows the DTA and TG curves of YAB complex. Complex is degraded mainly by three stage process. The first was decomposition at 63.3 ºC is caused by the loss of water in the structure and was determined to be 15.5 % (theoretically 15.8 %). These two values are consistent with each other and correspond to 6 moles of water. The product at 1000 °C is $Y_2O_3 + Na_2O$ and the mass left at 1000 ºC is 27 %. The theoretical amount left as a result of decomposition is 25.8 %. This value is quite consistent with the empirical results (Y_2O_3: m.p.: 2438 ºC, Na_2O: m.p.: 1132 ºC (dec)[30].

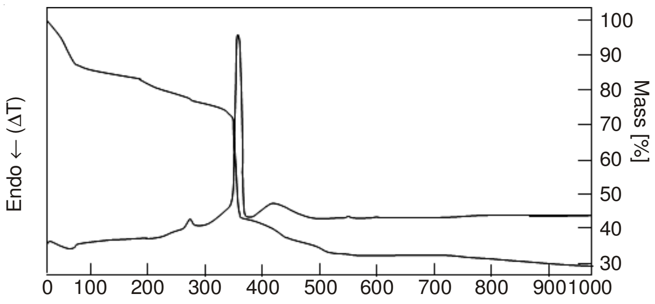

Fig. 5. DTA and TG Curves of the YAB Complex

Conclusion

In summary, potentiometric equilibrium measurements were performed at 25 ºC and an ionic strength of I = 0.1 M NaCl to determine the interaction of the polydentate ligand EDTA and 2,3-DHBA with Y(III) in a 1:1:1 ratio also mixed ligand complex of YAB have been synthesized and characterized.

As shown in the Table-2, the equilibrium constant of the reaction 3 is lower than the reaction 2.

$$Y^{3+} + B^{3-} \rightleftharpoons YB \qquad (2)$$

$$YA^{-} + B^{3-} \rightleftharpoons YAB^{4-} \qquad (3)$$

When the 2,3-DHBA binds to the YA^- complex as a secondary ligand to form a mixed ligand complex, there appear to be steric and electrostatic effects. Due to these two effects, the coordination of 2,3-DHBA to the YA is difficult than those of the coordination of 2,3-DHBA to the Y(III).

Coordination and/or crystal waters exist in the structure of the obtained complex. Because the 3500-3000 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 and 1678 cm^{-1} of the IR spectra of EDTA and 2,3-DHBA, respectively, shifted to 1601.4 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. The ^{1}H NMR spectra of YAB complex, the quartet peaks for acetate protons and the single peak for ethylene protons is observed. These peaks show acetate protons and ethylene protons of EDTA.

In the ^{1}H-NMR spectra of the YAB complex, peaks that the aromatic ring protons of 2,3-DHBA are seen at 7.19 ppm, 6.85 ppm and 6.63 ppm. The singlet peak belonging to OH protons in the meta- position to the carboxylate of 2,3-DHBA was observed at 8.33 ppm. Also, the peak belonging to the hydrogen bond between OH protons in the *ortho* position with the carboxylate oxygen is observed at 16.70 ppm. Consequently, it may be said that the binding between Y(III) and 2,3-DHBA is the carboxylate type. In the ^{13}C NMR spectrum of the mixed ligand complex of Y(III), the carboxylate carbons of EDTA are observed at 179.95 ppm, the carboxylate carbons of 2,3-DHBA are observed at 172.93 ppm. $-CH_2$ carbons linked to the carboxylate carbon of EDTA are observed at 62.50 ppm, whereas $-CH_2-$ carbons belonging to ethylenediamine of EDTA are observed at 57.52 ppm. In the ^{13}C NMR spectrum of the mixed ligand complex of Y(III), peaks at 151.57, 144.23, 121.41, 119.23, 118.54 and 118.38 ppm, belong to the carbons in the benzene ring. The ^{1}H$^-$ and ^{13} CNMR spectrum of YAB complex obtained contains both EDTA and 2,3-DHBA. Consequently, it may be said that the YAB complex formed. The results of the C, N and H analyses of the YAB complex indicates that the predicted structure is $Na_2[Y(C_{10}H_{15}N_2O_8)(C_7H_5O_4)(H_2O)].5H_2O$.

Wang *et al.*[3,7] determined in their study that the coordination number of Y(III) in the Y(III):EDTA complex is nine. In this case, in the YAB complex, Y(III) ion are coordinated by a hexzadendate EDTA, 2,3-DHBA that a bond in the carboxylate type and one water molecule whose formula is $Na_2[YAB(H_2O)].5H_2O$. It may be said that one of the six moles of water, which was suggested for the complex, was bound to Y(III) and the other five moles are present as hydrate water, *i.e.* $Na_2[YAB(H_2O)].5H_2O$. It is estimated that the geometry of the YAB mixed ligand complex formed with the Y(III) ion, which has a nine coordination number is the three-capped trigonal prizma.

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