

전이금속 착물들의 합성 및 결정구조 연구
(제 1 보) EDTA 와 IMDA 복합 킬레이트가 란탄족 원소들
(La, Nd, Gd, Ho, Yb)의 안정도 상수에 미치는 영향

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Studies on the Synthesis and Structure of Macrocyclic Complexes
for Transition Metals. (Part 1) Effects of Stability Constant on
the Co-formation of Mixed Chelates (EDTA and IMDA)
with Lanthanum (La, Nd, Gd, Ho, Yb)

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요 약. Ln-EDTA 1 : 1 착물과 IMDA 사이의 착물형성에 대한 안정도 상수들을 이온세기 $\mu=0.1M$, KNO_3 와 $20.0 \pm 0.2^\circ C$ 에서 전위차 적정법으로 연구하였다. Ln(EDTA)(IMDA) 혼합리간드 착물들에 비교적 큰 안정도 상수가 형성된다는 사실을 밝혔으며, Ln 원소들의 원자번호에 대한 형성도 상수들의 경향을 Ln 원소의 배위수와 반지름의 바탕에서 고찰하였다.

ABSTRACT. The formation constants of the complexes between Ln-EDTA 1 : 1 complex and IMDA have been investigated by a potentiometric titration method at 20.0 ± 0.2 degree C and $\mu=0.1(KNO_3)$. Unusually large stability in Ln(EDTA) mixed ligand complexes was found. Trends in the formation constants vs. atomic number of the lanthanide metals were discussed on the basis of coordination number and ionic radius of the metals.

INTRODUCTION

Lanthanide chemistry is initiated from the discovery of an unusual mineral specimen ytterbium by Carl Axel Arrhenius in 1787 and of a mineral cerite by Axel Fredrik Cronstedt in 1751.

The lanthanides or lanthanoids except Pm, were originally known as rare earths from their occurrence in phosphate rocks and oxide

(earth) mixture. There are not rare elements, and the absolute abundance in the lithosphere is relatively high.

Lanthanides are, strictly, the fourteen elements that follow lanthanum in Periodic Table and the fourteen 4f electrons are successively added to the lanthanum configuration.

Since these 4f electrons are relatively uninvolved in bonding, lanthanides can be usually high

Table 1. The properties of lanthanide, copper and zinc atoms and ions

Atomic number	Name	Symbol	Electronic Configuration		$E^0(V)$	Ionic Radius
			Atom	Ion		
57	Lanthanum	La	5d 6s ²	(xe)	-2.37	1.061Å
60	Neodymium	Nd	4f ⁴ 6s ²	4f ⁴	-2.32	0.995Å
64	Gadolinium	Gd	4f ⁷ 5d6s ²	4f ⁷	-2.29	0.938Å
67	Holmium	Ho	4f ¹¹ 6s ²	4f ¹⁰	-2.33	0.894Å
70	Ytterbium	Yb	4f ¹⁴ 6s ²	4f ¹⁴	-2.22	0.858Å
29	Copper	Cu	3d ¹⁰ 4s	3d ⁹	+0.337	87pm
30	Zinc	Zn	3d ¹⁰ 4s ²	3d ¹⁰	-0.762	88pm

Electronic configurations given above are only the valence shell electrons, that is, outside the (xe) shell for lanthanide and (Ar) shell for lanthanide and (Ar) shell for Cu and Zn. Ionic state is +3 for Ln and +2 for Cu and Zn. $E^0(V)$ is $M^{n+} + ne^- \rightarrow M$. Here $n=3$ for Ln, $n=2$ for Cu and Zn.

electropositive ions. The radii of these ions decrease with the increasing atomic number from lanthanum, thus constituting the lanthanide contraction¹. (Table 1)

The cause of this contraction is that the shielding of one 4f electron by another one. It is very imperfect because of the shapes of the orbitals, the effective nuclear charge experienced by each 4f electron increases in each case. Thus this effect causes a reduction in size of the entire 4f shell². But 4f orbitals are very effectively shielded due to the influence of external forces by the overlying 5s² and 5p⁶ shells. Hence there are only slightly affected by the surroundings and remain practically invariant for a given ion in all compound.

Oxidation state of lanthanides are usually tripositive because the sum of the first three ionization enthalpies is comparatively low. However, in aqueous solutions and in solids, quadrivalent ionic cerium can be obtained and divalent ionic samarium, europium, ytterbium, and thulium are also found. In solution, some divalent ionic elements are oxidized readily to tripositive ionic states³. The existence of these various oxidation states can be interpreted by consideration of ionization enthalpies, enthalpies

of sublimation of the metals, and lattice energies, etc.

The absence of extensive ligand interaction with the 4f orbital minimizes ligand field stabilization effects(LFSE) because lanthanides behave as typical hard acids. The lack of LFSE reduces overall stability but, on the other hand, provides a greater flexibility in geometry and

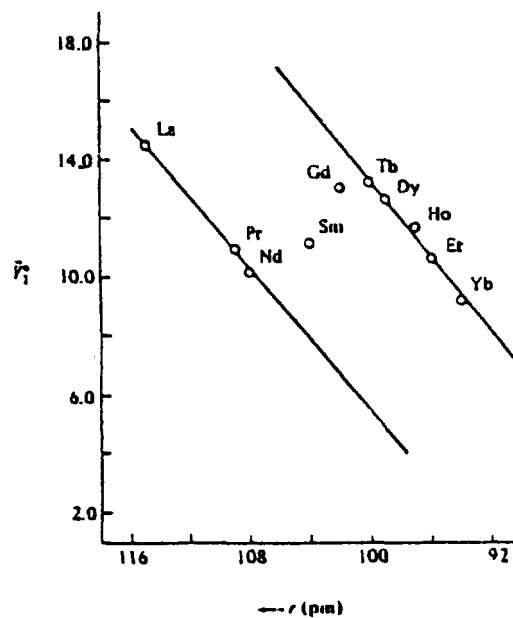


Fig. 1. Partial molal volume of hydrated Ln^{3+} . Lines represent 9- and 8- coordination. Sm^{3+} and Gd^{3+} exist as equilibria between the two species.^{6,7}

Table 2. Colors and term symbols of electronic ground states of the Ln³⁺ ions.

Ion	Color	Term symol
La ³⁺	Colorless	¹ S ₀
Nd ³⁺	Lilic	⁴ I _{9/2}
Gd ³⁺	Colorless	⁸ S _{7/2}
Ho ³⁺	Pink-yellow	⁵ I ₈
Yb ³⁺	Colorless	² F _{7/2}

coordination number since LFSE is not lost⁴.

It is believed that coordination number of lanthanides is larger than 6. Commonly accepted coordination numbers of lanthanides are 7, 8, or 9⁵. It was suggested that coordination number of lanthanide is 8 or 9. And Sm³⁺, Eu³⁺ or Gd³⁺ is transitional in coordination type^{6,7}. (Fig. 1)

The spin-orbit coupling constants of the 4fⁿ electrons are so quite large (order of 1000cm⁻¹), as the lanthanide ions have ground states with a single well-defined value of the total angular momentum. The colors and term symbols of electronic ground states of the Ln³⁺ ions are given in Table 2.

Their geometries are monocapped trigonal prism and monocapped octahedron at 7, square antiprism and dodecahedron at 8, and tricapped trigonal prism at 9^{1,8}.

However, there are some difficulties to separate these lanthanide ions each other. The origin of these difficulties lies on the ubiquitousness of the tripositive state and the only slight differences of the degree which a given property changes from ion to ion in this oxidation state.

Ion exchange is one of the separation methods. In as much as the affinity of the two ions Ln and Ln' for the resin sites does not differ markedly, elution by a simple cation is not effective in achieving separation. But, if a suitable complexing agent is added, differences

in the stability of the chelates formed with Ln and Ln' alter separation factor more favorable^{9,10}.

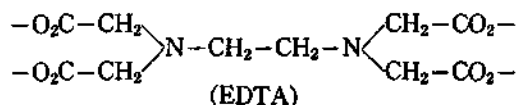
Stabilities of lanthanide complexes are usually influenced by ionic radius of lanthanide, coordination number of its cation and coordinating abilities of various donor atoms. In general case, they are influenced by combination of above factors¹¹.

Most of the studies on lanthanide complexes were purposed to separation. But nowadays, studies on coordination number of lanthanide complexes are increased significantly^{7,11,32}.

Various investigators have determined the formation constant of lanthanide complexes by a potentiometric pH titration method¹²⁻¹⁴, potentiometric pH and pM titration method^{15,16}, polarographic method¹⁷, spectroscopic method¹⁸, and proton magnetic resonance spectroscopic method³³, etc.

In recent years, the formation of lanthanide complexes containing two different ligands has become of interest to coordination chemists, and the coordination numbers and geometries of these complexes have been studied on the basis of the formation constant¹⁹⁻²¹.

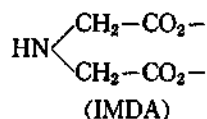
The tripositive lanthanide ions are well known to form highly stable 1:1 complexes Ln(EDTA)⁻ with ethylenediamine-tetraacetate (EDTA⁴⁻).



And the stability constants of these complexes have been determined by a number of authors²².

Since it was known that coordination number of Ln³⁺ ions is larger than six, on coordination with the hexadentate EDTA, there is a possibility that in the presence of the second ligand, mixed complexes will be formed.

In this study, formation constants between 1 : 1 complex of $\text{Ln}(\text{EDTA})^-$ and iminodiacetate (IMDA) as the second ligand were determined and the results were discussed on the basis of coordination number of the lanthanide metals.



Cu^{2+} and Zn^{2+} which have coordination number less than six were also studied to compare with Ln^{3+} ion.

EXPERIMENTAL

(i) Apparatus

The apparatus was consisted of titration cell with water jacket, a constant temperature bath, and a pump to circulate the water to maintain 20.0 ± 0.2 degree C.

Fisher accumet model 525 digital pH/ion meter equipped with Metrohm combination electrode (glass electrode and Ag/AgCl reference electrode) was used to measure the pH of solution to 0.001 digit.

pH meter was calibrated with standard nitric acid solutions which were conformed against standard potassium hydroxide solution. Ionic strength of the standard nitric acid solutions was adjusted to 0.1 by addition of 1.00M potassium nitrate²³.

(ii) Preparation of solutions

(a) *Lanthanide Nitrate Neutral Stock solutions.* Lanthanide nitrate neutral stock solutions, about 0.1 M in $\text{Ln}(\text{NO}_3)_3$, were prepared by dissolving the corresponding lanthanide oxides in slight excess of nitric acid. The solutions were evaporated to nearly dryness to remove the excess of nitric acid. The residues were redissolved in distilled water, and pH of the solutions was checked. These operations were continued until the solutions became neutral. These acid-deficient

solutions were then filtered to remove undissolved materials²⁴.

Aliquots of each of these solutions were analyzed for lanthanide metal content by oxalate precipitation and ignition at about 950 degree C.

The lanthanide oxides which were supplied by the lanthanide separation group at the Department of Chemistry, Seoul National University were 99.9% pure or better, and G.R. grade of nitric acid was used²⁵.

(b) *Ligand Buffer solutions.* Iminodiacetic acid (IMDA) was obtained from Aldrich Chemical Company, Inc., and G.R. grade acid form ethylenediaminetetraacetic acid (EDTA, H_4Y) was obtained from the Fisher Chemical Company. They were dried for 3 hours at about 100 degree C and used without further purification. The concentration of the solutions was mM order because solubility of acid form EDTA was to that extent.

(c) *Potassium Nitrate solution.* Reagent grade of potassium nitrate was obtained from Wako Pure Chemical Company. It was dried for 5 hours at about 100 degree C and used without further purification.

(d) *Copper and Zinc Nitrate Stock solution.* E.P. grade copper metal of Kanto Chemical Company and Reagent grade zinc metal of Kanto Chemical Company were obtained. These metals were washed with dilute nitric acid, dried and weighed exactly. The concentrations of the metals were calculated from these weights.

Their nitrate neutral stock solutions were prepared by the same method of the procedure described in lanthanide nitrate neutral stock solution except the analysis.

(e) *Standard Base solution (Potassium Hydroxide solution).* Potassium hydroxide stock solution was prepared by dissolving E.P. grade

reagent of Kanto Chemical Company in distilled water which had previously been boiled to remove dissolved carbon dioxide. The base was standardized against the known weight of potassium hydrogen phthalate.

(iii) Experimental

1.000mM of metal and ligand buffer solution were used. In one titration system, solutions having 1:1 concentration ratio of metal ion and EDTA were used. In the other, solutions having not 1:1 concentration ratio of metal ion, EDTA, and additional IMDA were used. Ionic strength of all solutions which were titrated was adjusted to 0.1 by addition of 1.00M potassium nitrate.

After equilibrium in a constant temperature bath for a day, solutions were titrated potentiometrically with potassium hydroxide solution bubbling with nitrogen gas for ten minutes.

(iv) Calculation^{26,27}

The calculation of the formation constants were carried out by the method given by Thompson and Loraas¹⁹



$$C_M = [MA]_t = [MA] + [MAB] \quad (2)$$

$$C_B = [B]_t = [H_2B] + [HB^-] + [B^{2-}] + [MAB] \quad (3)$$

$$a^*C_B + [H^+] - [OH^-] = [HB^-] + 2[B^{2-}] + 2[MAB] \quad (4)$$

Were A is EDTA, B is IMDA and a^* is moles of base added per mole of B in excess of the four moles needed to neutralize EDTA completely.

Reaction (1) assumed a equilibrium that IMDA as the second ligand coordinates to 1:1 complex of EDTA and metal ion. This assumption was possible because formation constants of EDTA to metal ions were much larger than that of IMDA. (Table 3)

Combining eq. 3 and eq. 4 gives the expres-

Table 3. Dissociation constants and formation constants of EDTA for metal ions (1:1 complex)²²

Metal ion	IMDA log K_1	EDTA
H ⁺ (pk ₁)	2.58	1.99
H ⁺ (pk ₂)	9.33	2.67
H ⁺ (pk ₃)	—	6.16
H ⁺ (pk ₄)	—	10.26
Ln ³⁺	5.88	15.50
Nd ³⁺	6.50	16.00
Gd ³⁺	6.68	16.60
Ho ³⁺	6.97	18.31
Yd ³⁺	7.42	19.39
Cu ²⁺	5.65	18.80
Zn ²⁺	5.14	16.51

ssion for [B]

$$[B] = \frac{(2-a^*)\{C_B - [H^+] + [OH^-]\}}{2X \frac{[H^+]^2}{k_1 k_2} + \frac{[H^+]}{k_2}}$$

Where k_1 and k_2 are the acid dissociation constants of B. (Table 3) Using this value of [B], eq. 2 and eq. 3 can be solved for [MA] and [MAB], respectively. Then the equilibrium constant for reaction (1) then is obtained easily.

$$K = \frac{C_B - [B] \left(\frac{[H^+]^2}{k_1 k_2} + \frac{[H^+]}{k_2} + 1 \right)}{[B] \{ C_M - C_B + [B] \left(\frac{[H^+]^2}{k_1 k_2} + \frac{[H^+]}{k_2} + 1 \right) \}}$$

RESULTS AND DISCUSSION

The potentiometric titration curves obtained on the equimolar mixture of metal ion (La, Nd, Gd, Ho, Yb, Zn, and Cu), EDTA and IMDA are illustrated in figure 2 to 8.

A consideration of titration curve shows that in lanthanide except Yb³⁺, there is a decided lowering of pH in higher buffer region when a mixture of the two ligands is titrated. But such kind of behavior is not observed in Cu²⁺, Zn²⁺, and Yb³⁺.

A lowering of pH in the high buffer region is indicative of the formation of a new kind of

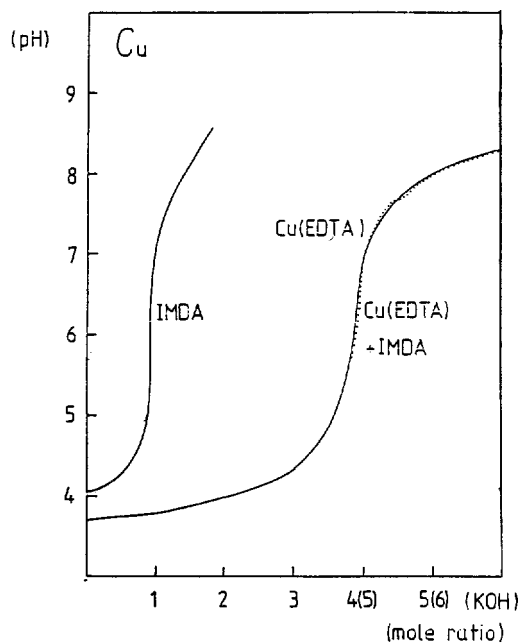


Fig. 2. Titration Curves for Cu(II).

complex species in the solution. As shown in Fig. 2 to 8, since mole ratio is 5 mixed ligand system, a very steep inflection occurs. It suggests that all four protons produced in the binding of EDTA to Ln^{3+} ion are neutralized at this point and a hydrogen from IMDA is also titrated. As additional base is added, a weak inflection is found when mole ratio is six. At this point, one hydrogen ion left in IMDA is dissociated, and the second ligand IMDA combines with $[\text{Ln}(\text{EDTA})]^-$ complex.

The species in solution at this point have nearly no affinity for H^+ or OH^- , (*i.e.*, the system has no buffering capacity) and it can be expected a stable mononuclear system is present, with the composition $(\text{Ln}(\text{EDTA})(\text{IMDA}))$, 1 : 1 : 1. The fact that a presence of the first inflection and the second inflection after subsequent buffer region can be explained by the difference in stability of the $[\text{Ln}(\text{EDTA})]^-$ and $[\text{Ln}(\text{IMDA})]^+$ complex species²⁸. (Table 3)

In Cu^{2+} and Zn^{2+} , addition of IMDA as a second ligand did not change the shape of titration curve. It can be explained from the formation of stable $[\text{M}(\text{EDTA})]^{2-}$ complex which does not form any additional mixed complex. And it is well known that the coordination number of these metals is six or less than six^{29,30}.

With experimental method used, it was not detected the formation of the mixed complex in Yb^{3+} , either.

The experimental data were analyzed on the basis of the assumption of a mixed chelate of the type MAB and calculated from averaging of seven potentiometric titration points.

The results which were obtained for the logarithms of the formation constants of these chelates corresponding to reaction(1) are listed in Table 4.

The data show that the stabilities of lanthanide are nearly the same from ion to ion through the series. However, they increase with increasing atomic numbers and have their maximum values in Nd^{3+} . For elements having atomic number greater than Nd, there are decrease in formation constants. Such a trend supports that the coordination number is not the same for the different

Table 4. Logarithms of formation constants. For $\text{M}(\text{EDTA})(\text{IMDA})$

$$K = \frac{[\text{M}(\text{EDTA})(\text{IMDA})]}{[\text{M}(\text{EDTA})][\text{IMDA}]}$$

$\mu = 0.1(\text{KNO}_3) \quad T = 20.0 \pm 0.2\text{C}$

Metal ion	log K
La^{3+}	4.25 ± 0.01
Nd^{3+}	4.64 ± 0.02
Gd^{3+}	4.47 ± 0.01
Ho^{3+}	4.04 ± 0.04
Yb^{3+}	—
Cu^{2+}	—
Zn^{2+}	—

*90% confidence level.

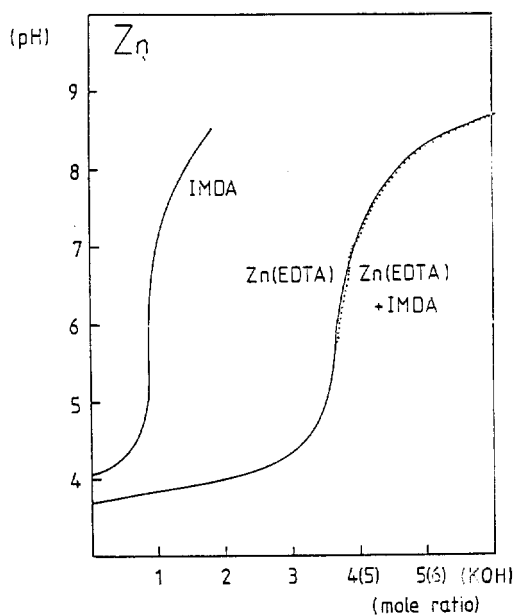


Fig. 3. Titration Curves for Zn(II).

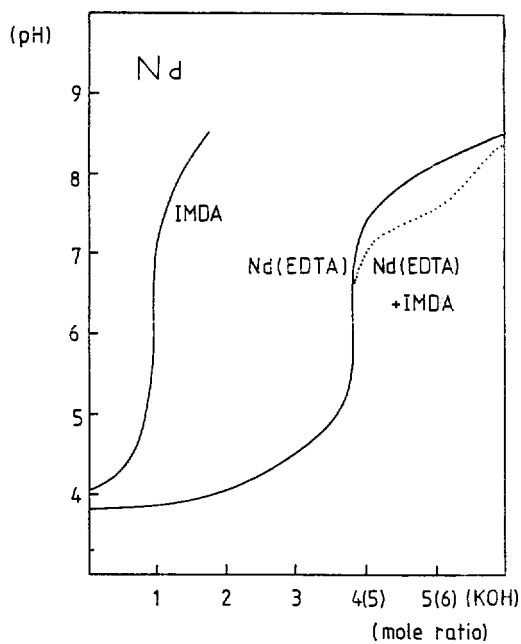


Fig. 5. Titration Curves for Nd(III).

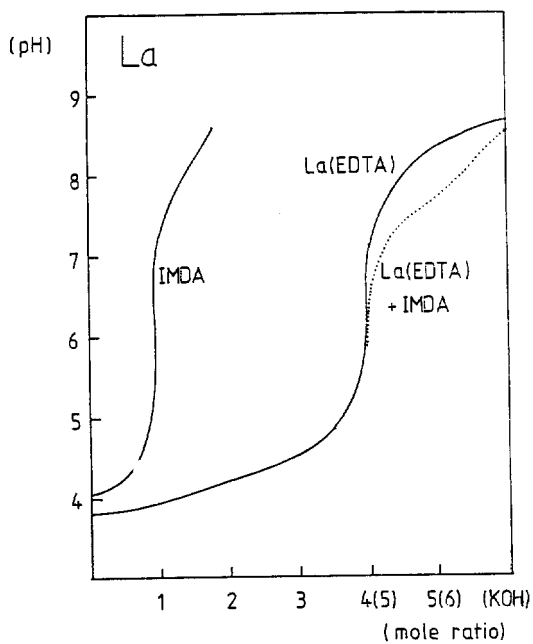


Fig. 4. Titration Curve for La(III).

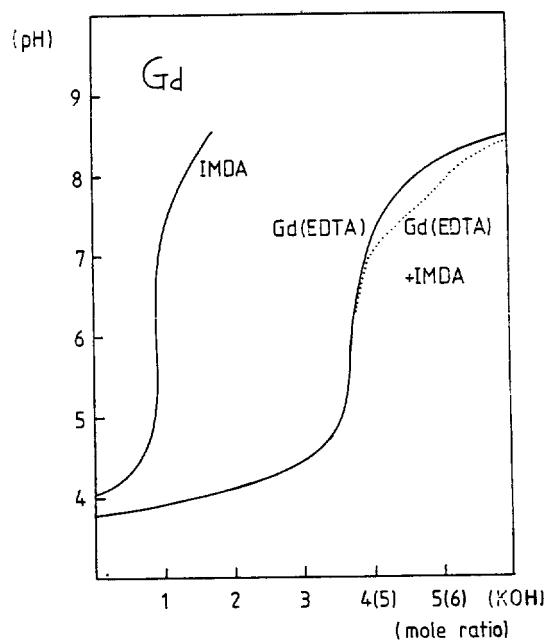


Fig. 6. Titration Curves for Gd(III).

Ln^{3+} ions but exhibits a break in the middle of the series probably decreasing from 9 to 8.

It is surmised that there is transition in the coordination type between Nd^{3+} and Eu^{3+} . This fact nearly agrees with existing thermodynamic

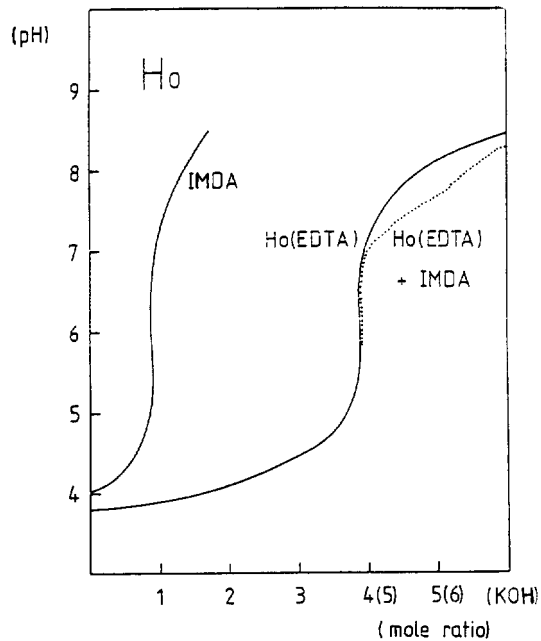


Fig. 7. Titration Curves for Ho(III).

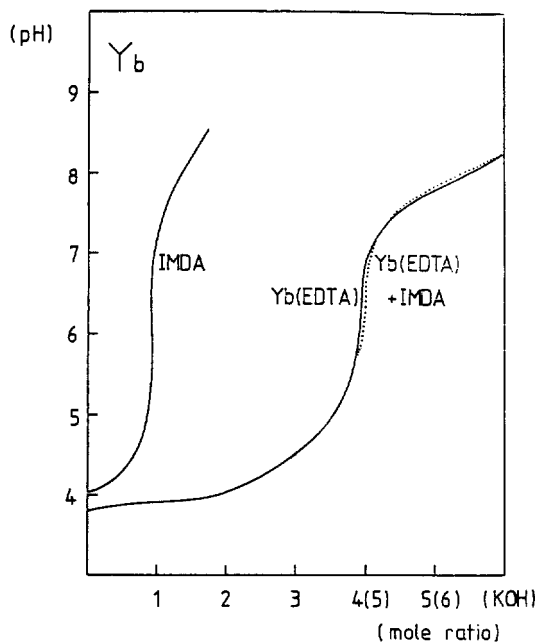


Fig. 8. Titration Curves for Yd(III).

data^{4,31}.

It was observed by Hoard *et. al.*⁷ that in the La-EDTA 1:1 complexes in aqueous media, EDTA is coordinated to the relatively large

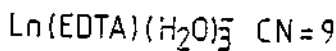
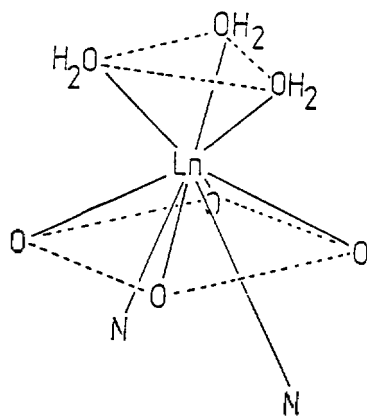


Fig. 9. $Ln(EDTA)(H_2O)_3$, when coordination number is nine⁷.

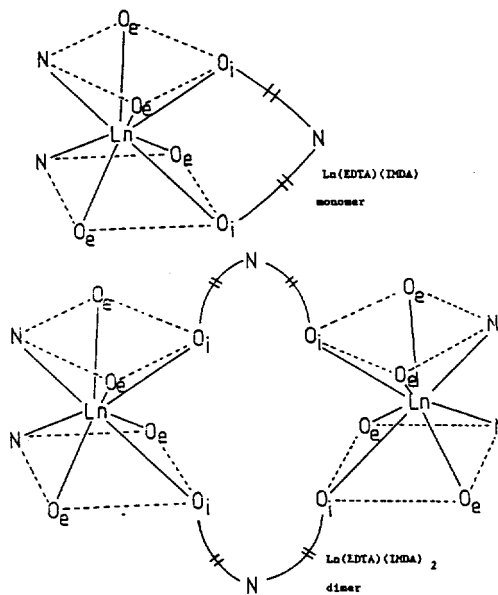


Fig. 10. Two possible arrangement when coordination number is eight. Monomer and dimer.

ions in a hemispherical shell and the other hemisphere is filled with three molecules of water. [Fig. 9]

These facts can be also applied to other light lanthanide having the coordination number of nine.

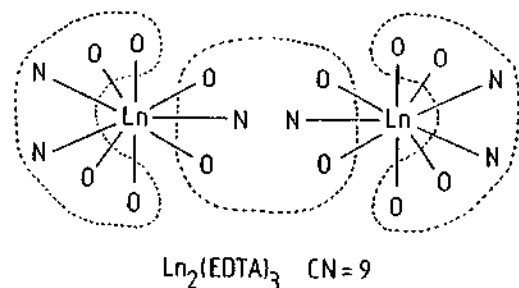
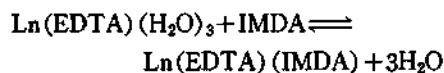


Fig. 11. Assumed structure of binuclear complex, $\text{Ln}_2(\text{EDTA})_3^{6+}$.

It is sufficient for three-dentate IMDA as a second ligand to occupy the space by substituting the three molecules of waters.



In the coordination number of nine in light lanthanide, there is no problem that IMDA occupies three coordination sites. However, in the case of coordination number of eight, only two coordination sites are possible. It is expected two carboxyl oxygen atoms of IMDA coordinate to Ln^{3+} ions because oxygen is the better donor than nitrogen. With experimental data, there is a significant stability in two site coordination.

But the case of Yb^{3+} can be explained that steric effects induced by shrinkage in ionic radius is more predominant than the coordination number and coulombic interaction.

In general, it is assumed that the simple compound formed will be a mononuclear in which each ligand bound contributes all of its donor groups to the same metal ion. An alternate possibility is that the pairs of bidentate ligands may bridge two metal ions to form a completely coordinated simple dimer. Two possible arrangements are illustrated in Fig. 11.

Ln-EDTA 1 : 1 complex has a negative charge, electrostatic repulsion toward the incoming second ligand IMDA was expected but it does

not prohibit their formation significantly.

EDTA is a duplicated IMDA shape. In Ln-EDTA system, with above observations, there is a possibility that not only Ln-EDTA 1 : 1 complex but 1 : 1.5 or 2 : 3 bridging complex is also formed. As a result of this study, we assumed two possible structures, which are given in Fig. 10 and 11.

CONCLUSION

There was the formation of mixed complex between Ln-EDTA 1 : 1 complexes and IMDA, but it was not observed in Yb-EDTA . The order of the stability of the mixed ligand complexes was below.



In Cu-EDTA and Zn-EDTA , they did not form additional mixed ligand complexes.

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