

## 거대고리 아자크라운화합물과 전이금속 및 란탄족금속이온의 착물의 안정도

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## The Stability Constant of Transition and Lanthanide Metal Ions Complexes with 15 Membered Macrocyclic Azacrown Ligands

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**요 약.** 새로운 아자크라운 화합물인, 1,4-dioxa-7,10,13-triazacyclopentadecane-N,N',N''-triacetic acid, N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**)과 1,4-dioxa-7,10,13-triazacyclopentadecane-N,N',N''-tripropiolic acid, N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**)는 이와 유사한 화합물의 합성방법을 수정하여 합성하였다. 합성된 이 아자크라운 화합물, N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>와 N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>의 양성자화 상수값은 전위차법을 이용하여 PKAS 프로그램으로부터 측정되어졌다. 그리고 0.1 M NaClO<sub>4</sub> 수용액으로 이온강도를 조절하고, 25 ± 0.1 °C에서 란탄족금속인, Ce<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup> 및 Yb<sup>3+</sup>과 리간드인 N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>와 N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>의 착물의 안정도상수를 전위차법을 이용하여 BEST 프로그램으로부터 구하였고, 또한 위와 같은 조건에서 전이금속인 Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> 및 Zn<sup>2+</sup>와 리간드인, N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>와 N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>의 착물의 안정도상수 값도 전위차법을 이용하여 BEST 프로그램으로부터 측정하였다. 합성된 아자크라운 화합물과 골격구조가 유사하고 아세트산과 프로피온산기를 포함하는, 1,7-dioxa-4,10,13-triazacyclopentadecane-N,N',N''-triacetic acid과 1,7-dioxa-4,10,13-triazacyclopentadecane-N,N',N''-tripropiolic acid의 착물의 안정도를 비교분석하였다.

**주제어:** 아자크라운 화합물, 안정도 상수

**ABSTRACT.** The azacrown compounds, 1,4-dioxa-7,10,13-triazacyclopentadecane-N,N',N''-triacetic acid, N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**) and 1,4-dioxa-7,10,13-triazacyclopentadecane-N,N',N''-tripropiolic acid, N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**) were synthesized by modified methods. Potentiometry was used to determine the protonation constant of the N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub> and N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>. The stability constants of complexes of the trivalent metal ions of Ce<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, and Yb<sup>3+</sup> and divalent metal ions of Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> with the ligands N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub> and N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub> have been determined at 25 ± 0.1 °C in 0.1 M NaClO<sub>4</sub> solution by potentiometric methods. The metal ion affinities of the two triazamacrocyclic ligands with three pendant acetate or propionate groups are compared to those obtained for the similar ligands, 1,7-dioxa-4,10,13-triazacyclopentadecane-N,N',N''-triacetic acid, and 1,7-dioxa-4,10,13-triazacyclopentadecane-N,N',N''-tripropiolic acid. The trends in stability of complexes for different metal ions due to changes in the nitrogen position of the donor atoms of the ligand are discussed.

**Keywords:** Azacrown Compound, Stability Constant

## INTRODUCTION

In recent years, there has been growing interest in the azacrown macrocyclic compounds which contain both oxygen and nitrogen donors.<sup>14</sup> Some of the azacrown compounds and metal complexes formed are of potential interest in medical applications,<sup>4,5</sup> in particular as NMR imaging agents.<sup>6</sup> This series of ligands have three or four nitrogen atoms in a macrocyclic ring with acetate, n-propionate, or iso-propionate linked to each. Some also have ether oxygen atoms forming 12- to 18-membered macrocyclic rings. Their complexation have been studied with the divalent transition metal ions (e.g., Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup>)<sup>7</sup>, and trivalent metal ions (e.g., Al<sup>3+</sup>, Ga<sup>3+</sup>, In<sup>3+</sup>, Fe<sup>3+</sup>, and Ln<sup>3+</sup> ions).<sup>7,8</sup>

These macrocyclic ligands provide an opportunity to study the influence of the size of the azacrown ring, of the change of N-pendent arms, and of the increasing number of donor atoms on the stability and selectivity of the metal complexes. The 1,7-dioxa-4,10,13-triazacyclopentadecane-N,N',N''-tri-acetic acid, N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>a</sub>**) and 1,7-dioxa-4,10,13-triazacyclopentadecane-N,N',N''-tripropionic acid, N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>b</sub>**) were synthesized earlier, and the protonation and stability constants with Ce<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, Yb<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> been determined previously.<sup>9,12</sup>

In this work, the 1,4-dioxa-7,10,13-triazacyclopentadecane-N,N',N''-tri-acetic acid, N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**) and 1,4-dioxa-7,10,13-triazacyclopentadecane-N,N',N''-tripropionic acid, N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**) were synthesized by a simpler procedure and a different method of alkylation with good yield. These ligands have three nitrogen atoms in macrocyclic ring with acetate or propionate groups linked to each of nitrogen. The objective of this research is to determine the protonation of the **II<sub>a</sub>** and **II<sub>b</sub>** and the stability constants with divalent and trivalent metal ions. These values are compared with those of N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>a</sub>**) and N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>b</sub>**) which differ in the position of the nitrogen and ether oxygen atoms in the macrocyclic ring.

## EXPERIMENTAL

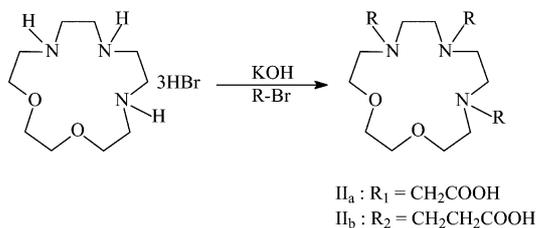
**Material and Standards Solution.** The reagents used in the synthesis, bromoacetic acid, 3-bromopropionic acid, triethyleneglycol, and triethylenamine were obtained from Aldrich Co. They were used as supplied without further purification and Dowex-50(8%) ion exchange resin (Sigma) was treated with 2 M NaOH aqueous solution to convert it to the OH form.

The concentration of **II<sub>a</sub>** and **II<sub>b</sub>** stock solution were determined by complexometric titration with a standardized Cu(ClO<sub>4</sub>)<sub>2</sub> solution using murexide as an indicator. The stock solutions of transition metal ions (Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup>) and of lanthanide metal ions (Ce<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, and Yb<sup>3+</sup>) were prepared from the corresponding metal chlorides or oxides (Aldrich, 99.9%) and were standardized by titration with Na<sub>2</sub>H<sub>2</sub>EDTA using murexide as an indicator.

**Apparatus.** The proton NMR spectra were measured on a DPX-300 FT-NMR spectrometer and the Elemental analyses were performed on a Perkin-Elmer. The protonation constants of the ligands were determined by pH potentiometry at 25±0.1 °C using a Radiometer Copenhagen Model TM 90 pH meter with a combination PHC 4400 pH electrode.

**Synthetic Procedures.** 1,4-dioxa-7,10,13-triazacyclopentadecane-N,N',N''-trihydrobromide was prepared by the procedures<sup>13</sup>, N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**) and N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**) were synthesized according to the modified methods of Krespan & Vogtle.<sup>9,14</sup> The synthetic route of these azacrown compounds is shown in *Scheme 1*.

**N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**).** Potassium hydroxide 0.79 g were added to a suspension of 1.85 g of 1,4-dioxa-7,10,13-triazacyclopentadecane-N,N',N''-trihydrobromide in 40 mL of absolute ethanol, and the mixture was stirred at room temperature for about 1 hour. The KBr precipitate was removed by filtration, and the solvent by vacuum distillation. The white residue obtained was dissolved in 20 mL of water. Bromoacetic acid (1.86 g, 13.2 mmol) was dissolved in 20 mL of cold water (1~2 °C). A solution of 1.7 g of KOH in 20 mL of water was added



Scheme 1. Synthetic route of N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II**<sub>a</sub>) and N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II**<sub>b</sub>).

dropwise (to form the bromoacetate) at 2~5 °C until a pH of 12 was reached. The [15]ane N<sub>3</sub>O<sub>2</sub> and BrCH<sub>2</sub>COOK solutions were mixed and heated to 48~50 °C. The remainder of the KOH aqueous solution described above was used to maintain the pH of the reaction solution at 11~12. The reaction solution was kept at 48~50 °C for 6 hr and then at room temperature for 18 hr. The solution was adjusted to pH 9.0 with 6 M HCl aqueous solution, and concentrated to about 10 mL by evaporation. The concentrated solution was loaded on a 15×300 mm column of the Dowex-50 ion exchange resin (OH<sup>-</sup> form). Successively, 200 mL of water, 200 mL of 0.01 M HCl aqueous solution, and 300 mL of 0.1 M HCl aqueous solution were passed through the column. The eluate, pH ca. 3, contained 0.82 g of the pure N-ac<sub>3</sub>[15]ane N<sub>3</sub>O<sub>2</sub>(**II**<sub>a</sub>). After elution with 100 mL of 0.2 M HCl aqueous solution, 1,4-dioxo-7,10,13-triazacyclopentadecane-N,N',N''-triacetic acid tri-HCl salt was obtained at 65%. The NMR spectral data were <sup>1</sup>H NMR(D<sub>2</sub>O-NaOD, pD=13.2): δ 3.58(t, 8H, -CH<sub>2</sub>-O-CH<sub>2</sub>-), 3.21 and 3.17(two s, 6H, -CH<sub>2</sub>-COO-), 2.75(t, 4H, -OCH<sub>2</sub>CH<sub>2</sub>N-), 2.61(s, 8H, -NCH<sub>2</sub>CH<sub>2</sub>N-). Anal calcd for C<sub>16</sub>H<sub>29</sub>N<sub>3</sub>O<sub>8</sub>·3HCl(%): C, 43.44; H, 7.29; N, 9.97; Cl, 24.04; found: C, 43.20; H, 7.24; N, 9.85; Cl, 23.92.

**N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II**<sub>b</sub>).** By a procedure similar to that described above N-ac<sub>3</sub>[15]ane N<sub>3</sub>O<sub>2</sub>(**II**<sub>a</sub>) 2.02 g yielded this product; yield 60%; <sup>1</sup>H NMR(D<sub>2</sub>O-NaOD, pD=13.2): 3.73(t, 8H, -CH<sub>2</sub>OCH<sub>2</sub>-), 3.25(t, 4H, -OCH<sub>2</sub>CH<sub>2</sub>-N), 2.55(s, 8H, -NCH<sub>2</sub>CH<sub>2</sub>N-), 2.69(t, 6H, N-CH<sub>2</sub>CH<sub>2</sub>COO-), 2.50(t, 6H, N-CH<sub>2</sub>CH<sub>2</sub>COO-). Anal calcd for C<sub>19</sub>H<sub>35</sub>N<sub>3</sub>O<sub>8</sub>·3HCl: C, 47.10; H, 7.90; N, 8.67; Cl, 21.95; found: C, 46.95; H, 7.81; N, 8.45; Cl, 21.63.

### Potentiometric Equipment and Calculation of Equilibrium Constants.

The protonation constants of ligands (**II**<sub>a</sub>) and (**II**<sub>b</sub>) were determined by pH potentiometry at 25±0.1 °C using a 50 mL glass-jacketed titration vessel completely sealed from the atmosphere. The temperature was controlled with the Haake thermostat and circulation of thermostated water through the jacket. CO<sub>2</sub> was excluded from the vessel during the titration by passing purified He gas through the titration vessel. The standard base or acid was added through a capillary tip placed below the surface of the Metrohm piston burette. Before use for measurements of the protonation constants and stability constants, the pH meter (±0.0001 pH unit) and electrode system were calibrated using standard, dilute HCl aqueous solutions at an ionic strength of 0.1 M (NaClO<sub>4</sub> solution) in the thermostated vessel at 25.0±0.1 °C.

The potentiometric data measurements were made on 10 mL of ligand solutions, 2.0×10<sup>-3</sup> M, diluted to a final volume of 20.0 mL, first in the absence of metal ions and in the presence of metal ion for which concentration ratios of ligand:metal ion of 1:1 for lanthanide and 1:2 for transition metals were used. The reaction mixture was titrated with 6.77×10<sup>-2</sup> M KOH solution in 0.05 mL increments. All titrations were performed two or three times, and reproducible results were obtained. The protonation constants ( $K_i^H = [H_iL]/[H_{i-1}L][H^+]$ ) were calculated by fitting the potentiometric data to the PKAS program.<sup>15</sup> The value of  $K_w = 10^{-13.78}$  used in the computation. The stability constants of the complexes formed in the aqueous solution were obtained by analysis of the experimental data using the BEST program.<sup>15</sup>

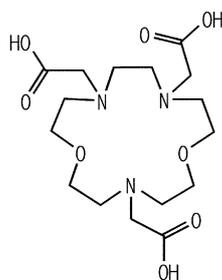
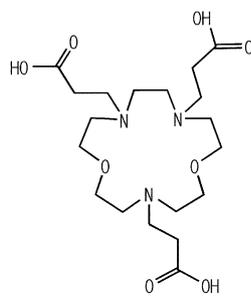
## RESULTS AND DISCUSSION

**Protonation constants.** The values of the stepwise protonation constants of ligands(N-ac<sub>3</sub>[15]ane N<sub>3</sub>O<sub>2</sub>(**II**<sub>a</sub>) and N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II**<sub>b</sub>)) obtained at 25±0.1 °C are listed in Table 1 together with the values determined previously for N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I**<sub>a</sub>) and N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I**<sub>b</sub>).

Table 1. Protonation constants ( $\log K_i^H$ ) of 15-membered macrocyclic ligands at  $25 \pm 0.1$  °C Protonation constants ( $\log K_i^H$ )

Equilibrium quotient	N-ac <sub>3</sub> [15]aneN <sub>3</sub> O <sub>2</sub> ( <b>I<sub>a</sub></b> ) <sup>a</sup>	N-pr <sub>3</sub> [15]aneN <sub>3</sub> O <sub>2</sub> ( <b>I<sub>b</sub></b> ) <sup>b</sup>	N-ac <sub>3</sub> [15]aneN <sub>3</sub> O <sub>2</sub> ( <b>II<sub>a</sub></b> ) <sup>c</sup>	N-pr <sub>3</sub> [15]aneN <sub>3</sub> O <sub>2</sub> ( <b>II<sub>b</sub></b> ) <sup>c</sup>
	0.1 M KCl	0.1 M NaClO <sub>4</sub>	0.1 M NaClO <sub>4</sub>	0.1 M NaClO <sub>4</sub>
$\frac{[H_2L]}{[L][H]}$	9.55	8.16	8.41	9.04
$\frac{[H_2L]}{[HL][H]}$	8.92	7.14	7.95	7.92
$\frac{[H_3L]}{[H_2L][H]}$	4.51	4.79	6.50	4.49
$\frac{[H_2L]}{[H_3L][H]}$	1.59	-	4.74	4.18

<sup>a</sup>From Ref 3, <sup>b</sup>From Ref 4, <sup>c</sup>This work

N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>a</sub>**)N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>b</sub>**)

Ethylenediaminetetraacetic acid is commonly shortened to EDTA. The dissociation constants for the EDTA are  $K_1=1.02 \times 10^{-2}$ ,  $K_2=2.14 \times 10^{-3}$ ,  $K_3=6.92 \times 10^{-7}$ , and  $K_4=1.02 \times 10^{-11}$ , and the dissociation constants for N-ac<sub>3</sub>[12]aneN<sub>3</sub> have three values.<sup>16,17</sup> It is of interest that the first two constants are of the same order of magnitude, which suggests that the two protons involved dissociate from opposite ends of the rather long molecule. As a consequence of their physical separation, the negative charge created by the first dissociation does not greatly inhibit the removal of the second proton. The same cannot be said for the dissociation of the other two protons, however, which are much closer to the negatively charged carboxylate ions created by the initial dissociation. When N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**) and N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**) are dissolved in water, they behave like the EDTA.

For The 12-membered macrocycle, 1-oxa-4,7,10-triazacyclodecane-N,N',N''-triacetic acid, NMR spec-

troscopy titration has shown<sup>10</sup> that the two higher values of the protonation constants correspond to nitrogen atoms, but the third and fourth correspond to protonation constants of the N-pendent carboxylate groups. The protonation constants of the N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**), 8.41, and 7.95, correspond to protonation of the nitrogen atoms, and the lower values, 4.74 and 6.50, to the carboxylate group. The two high values of the protonation constants of the N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**), 9.04 and 7.92, are related to nitrogen protonation, and the lower values, 4.49 and 4.18, to carboxylate oxygen protonations. N-pro<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**) protonation has the same pattern as that of 1-oxa-4,7,10-triazacyclodecane-N,N',N''-triacetic acid, as protonation of the nitrogen atoms have higher constants than the N-pendent carboxylate groups.

The basicity of N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>a</sub>**) is higher than that of N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>b</sub>**), but the values of N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**) are smaller than those of N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**), although both have a 15-membered ring. The structural differences of N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>a</sub>**) or N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>b</sub>**) and N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**) or N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**) involve a nitrogen atom of N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>a</sub>**) or N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>b</sub>**) separated by longer chains (-CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-) and a less rigid ring of those azacrown compounds. This is due to steric effects and decreasing coulombic interaction between the nitrogen atoms unseparated by longer chains and carboxylate groups. The complexes of the metal ions with N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**)

are expected to be more stable than the metal complexes of the N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**) due to their comparative basicity values.

**Stability Constants of Transition Metal Ions.**

The stability constants of the transition metal ion complexes with N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**) and N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**) are listed in Table II. In this table, the literature values for the same metal ions with ligands N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>a</sub>**) and N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>b</sub>**) are listed also for comparison.<sup>18,19</sup> The analysis by the BEST indicates that all. These ligands form the ML complex, some form protonated complex species and binuclear species are formed. However, due to the large uncertainties of the constants for such temporary complexes, only the logβ<sub>101</sub> values are reported.

The values of the stability constants of transition metal ion complexes formed with the N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**) are higher than those with N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**), even though these ligands have the same number of donor atoms and ring size. The increase in stability for this complex can be interpreted as due to a more favorable steric arrangement of the ligands about the metal ion, and it account to the higher overall basicity of the N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**) than N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**) as shown in Table 2.

In Table 2 are shown that the order of the stability constants of the transition metal ion complexes with the N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**) and N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**) follows the Irving-Williams series.<sup>20</sup> The relatively large stability constant value of Cu<sup>2+</sup> is due to the

extra stabilization of its complex by Jahn-Teller distortion. The transition metal complexes formed with the N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**) are stable than those with the N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**), because the N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**) are provided to flexibility for binding of cation metals. The values of the stability constants do not provide enough information to indicate more detail about the nature of the complexes formed. The determination of the thermodynamic functions and some X-ray structures would be necessary to provide further insights.

**Stability Constants of lanthanide metal Ions.**

The stability constants of complexes formed by N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**) and N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**) with Ce<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, and Yb<sup>3+</sup> have been determined in 0.1 M NaClO<sub>4</sub> ionic medium at 25±0.1 °C. The values obtained can be seen in Table 3, together with the values determined in the previous work for N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>a</sub>**) and N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**I<sub>b</sub>**).<sup>4</sup> The logarithm stability constants, logβ<sub>101</sub> of the complexes formed by N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>a</sub>**) with trivalent metal ions have been determined on 9.26 for Ce<sup>3+</sup>, 11.85 for Eu<sup>3+</sup>, 9.98 for Gd<sup>3+</sup>, and 9.74 for Yb<sup>3+</sup>, and those of the complexes formed by N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(**II<sub>b</sub>**) with Ce<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, and Yb<sup>3+</sup> have been determined on 16.49 for Ce<sup>3+</sup>, 16.74 for Eu<sup>3+</sup>, 16.57 for Gd<sup>3+</sup>, and 16.85 for Yb<sup>3+</sup>. The much larger ionic radius is reflected in lower values of stability constants, as one would predict for mainly electrostatic complexes. Similarly, the values of the stability constants on lanthanide metal ions with the ligand are increasing according to atomic number,

Table 2. Stability Constants (logβ<sub>101</sub>) for the Metal Complexes of 15-membered Macrocyclic Ligands with Transition Metal Ions at 25±0.1 °C

Cation	Quotient	N-ac <sub>3</sub> [15]aneN <sub>3</sub> O <sub>2</sub> ( <b>I<sub>a</sub></b> ) <sup>a</sup>	N-pr <sub>3</sub> [15]aneN <sub>3</sub> O <sub>2</sub> ( <b>I<sub>b</sub></b> ) <sup>b</sup>	N-ac <sub>3</sub> [15]aneN <sub>3</sub> O <sub>2</sub> ( <b>II<sub>a</sub></b> ) <sup>c</sup>	N-pr <sub>3</sub> [15]aneN <sub>3</sub> O <sub>2</sub> ( <b>II<sub>b</sub></b> ) <sup>c</sup>
Co <sup>2+</sup>	$\frac{[ML]}{[M][L]}$	16.38	13.61	10.36	16.87
Ni <sup>2+</sup>	$\frac{[ML]}{[M][L]}$	14.94	14.12	10.50	16.97
Cu <sup>2+</sup>	$\frac{[ML]}{[M][L]}$	17.54	12.79	10.81	17.25
Zn <sup>2+</sup>	$\frac{[ML]}{[M][L]}$	16.38	13.93	10.40	16.46

<sup>a</sup>From Ref 3, <sup>b</sup>From Ref 4, <sup>c</sup>This work

Table 3. Stability Constants ( $\log\beta_{101}$ ) for the Metal Complexes of 15-membered Macrocyclic Ligands with Lanthanide Ions in 0.1 M NaClO<sub>4</sub> at 25±0.1 °C

Cation	Quotient	N-meac <sub>3</sub> [15]aneN <sub>3</sub> O <sub>2</sub> (I <sub>a</sub> ) <sup>a</sup>	N-pr <sub>3</sub> [15]aneN <sub>3</sub> O <sub>2</sub> (I <sub>b</sub> ) <sup>b</sup>	N-ac <sub>3</sub> [15]aneN <sub>3</sub> O <sub>2</sub> (II <sub>a</sub> ) <sup>c</sup>	N-pr <sub>3</sub> [15]aneN <sub>3</sub> O <sub>2</sub> (II <sub>b</sub> ) <sup>c</sup>
		Ce <sup>3+</sup>	$\frac{[ML]}{[M][L]}$	11.26	10.94
Eu <sup>3+</sup>	$\frac{[ML]}{[M][L]}$	11.55	11.66	11.85	16.74
Gd <sup>3+</sup>	$\frac{[ML]}{[M][L]}$	11.49	11.23	9.98	16.57
Yb <sup>3+</sup>	$\frac{[ML]}{[M][L]}$	11.80	11.96	9.74	16.85

<sup>a</sup>From Ref 19, <sup>b</sup>From Ref 4, <sup>c</sup>This work

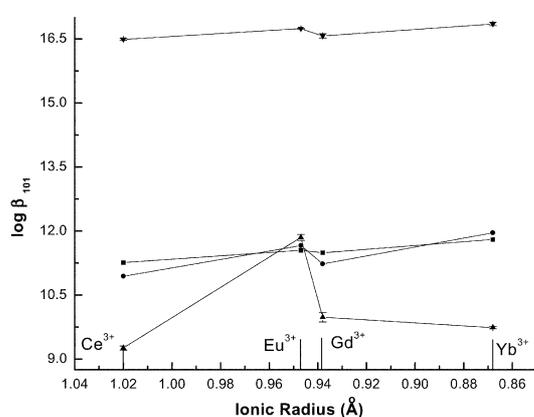


Fig. 1. Variation of the stability constants for the metal complexes of macrocyclic ligands with the ionic radius of the trivalent metal ions; ■— N-meac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(I<sub>a</sub>), ●— N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(I<sub>b</sub>), ▲— N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(II<sub>a</sub>), and ▼— N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(II<sub>b</sub>).

due to increase of acidity. However, the value of stability constant of Gd<sup>3+</sup> ion is less than that of Eu<sup>3+</sup> ion. This disorder behavior is also reported by Moeller<sup>21</sup>.

The metal complexes formed with N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(II<sub>b</sub>) are considerably more stable than those formed with macrocyclic ligands(N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(II<sub>a</sub>), N-ac<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(I<sub>a</sub>), and N-pr<sub>3</sub>[15]aneN<sub>3</sub>O<sub>2</sub>(I<sub>b</sub>)). This is due to the N-pendent arms of the propionate and the steric structure of ligand which allow better packing around the metal ions.

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