Stability Constants of First-row Transition Metal and Trivalent Lanthanide Metal Ion Complexes with Macrocyclic Tetraazatetraacetic and Tetraazatetramethylacetic Acids

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The protonation constants of the macrocyclic ligands, 1,4-dioxa-7,10,13,16-tetraaza-cyclooctadecane-N,N',N'', N'''-tetra(acetic acid) [N-ac_4[18]aneN_4O_2] and 1,4-dioxa-7,10,13,16-tetraazacyclooctadecane-1,4-dioxa-7,10,13,16-N,N',N'',N'''-tetra(methylacetic acid) [N-$meac_4$[18]aneN_4O_2] have been determined by using potentiometric method. The protonation constants of the N-ac_4[18]aneN_4O_2 were 9.31 for $\log K_1^H$, 8.94 for $\log K_2^H$, 7.82 for $\log K_3^H$, 4.48 for $\log K_4^H$ and 2.94 for $\log K_5^H$. And the protonation constants of the N-$meac_4$[18]-aneN_4O_2 were 9.34 for $\log K_1^H$, 9.13 for $\log K_2^H$, 8.05 for $\log K_3^H$, 5.86 for $\log K_4^H$, and 3.55 for $\log K_5^H$. The stability constants of complexes on the divalent transition ions (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) and trivalent metal ions (Ce^{3+}, Eu^{3+}, Gd^{3+}, and Yb^{3+}) with ligands N-ac_4[18]-aneN_4O_2 and N-$meac_4$[18]aneN_4O_2 have been obtained from the potentiometric data with the aid of the BEST program. The three higher values of the protonation constants for synthesized macrocyclic ligands correspond to the protonation of nitrogen atoms, and the fourth and fifth values correspond to the protonation of the carboxylate groups for the N-ac_4[18]aneN_4O_2 and N-$meac_4$[18]aneN_4O_2. The meatal ion affinities of the two tetra-azamacrocyclic ligands with four pendant acetate donor groups or methylacetate donor groups are compared. The effects of the metal ions on the stabilities are discussed, and the trends in stability constants resulting from changing the macrocyclic ring with pendant donor groups and acidity of the metal ions.

Introduction

Macrocyclic polyethers, polyoxapolyaza and polyazapoly-carboxylates have the remar-kable property of complexing selectivity with alkaline-earth or first-row transition m-etal (II) ions such that intensive efforts have been made in their applications to analy-tical chemistry, biochemistry, hydrometallurgy, and waste treatment. Several factors influence the thermodynamic and kinetic stabilities of metal complexes of macrocyclic ligands. These factors are the size of the metal ion and the ligand topology, such as charge, cavity size, number of donor atoms, and stereochemical rigidity.[1~8]

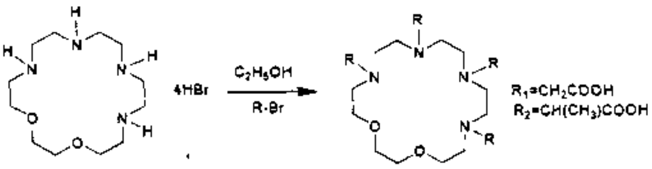
Kim and Hong[9] reported the stability constants of divalent transition and trivalent lanthanide metal ion complexes with macrocyclic 1,7-dioxa-4,10,13-triazacyclopentade-cane-4,10,13-tri(methylacetic acid) and 1,7,13-trioxa-4,10,16-triazacy-clooctadecane-4,10,16-tri(methylacetic acid). These series of ligands having acetate groups as N-pendant arm provide an opportunity to study the influence of size of the macrocyclic ring and the increasing number of donor atoms to the stability and selectivity of metal com-plexes.[10]

We initiated this project in order to understand how protonation constants and sta-bility constants of first-row transition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) and triva-lent lanthanide metal ions (Ce^{3+}, Eu^{3+}, Gd^{3+}, and Yb^{3+}) complexes are affected by the size of metal ions and the number of donor atoms, the chelate ring and cavity size of synthesized 1,4-dioxa-7,10,13,16-tetraazacyclooctadecane-N,N', N'',N'''-tetraacetic acid, N-ac_4[18]aneN_4O_2 and 1,4-dioxa-7,10,13,16-tetraazacyclooctadecane-1,4-Dioxa-7,10,13,16-N,N',N'',N'''-tetramethylacetic acid, N-$meac_4$[18]aneN_4O_2.

Experimental Section

Meterals. The reagents used to synthesis, Dowex 1×8 ion exchange resin and sil-icagel (200-400 mesh, 60 Å) were obtained from Aldrich Chemical Co. The concentr-ations of N-ac_4[18]aneN_4O_2 and N-$meac_4$[18]aneN_4O_2 stock solutions were determined by titrating against a standard $Cu(ClO_4)_2$ solution using murexide as an indicator. The stock solutions of first-row transition metal ions(II) and trivalent lanthanide metal ions(II) were prepared from the metal chloride or metal oxide (Aldrich, 99.9%) and their concentrations determined by Na_2H_2EDTA titrations using murexide as an indicator. All other chemicals were used analytical grade without further purification. All solutions were prepared in deionized water.

Synthesis of N-ac_4[18]aneN_4O_2 and N-$meac_4$[18]ane N_4O_2. 1,4-dioxa-7,10,13,16-tetraazacyclooctadecane-N,N',N'',N'''-tetrahydrobromide was prepared by previously reported procedures.[11~14] N-ac_4[18]aneN_4O_2 and N-$meac_4$-[18]aneN_4O_2 were synthesized according to the methods of Martell *et al.*[10,15,16] and Kim *et al.*[17] The synthetic route of N-$meac_4$ [18]aneN_4O_2 and N-ac_4[18] aneN_4O_2 was shown in Scheme 1.



Scheme 1. Synthetic route of N-meac$_4$[18]aneN$_4$O$_2$ and N-ac$_4$[18]-aneN$_4$O$_2$.

The potassium hydroxide (87%) pellets, 0.77 g (12 mmol) were added to suspension of 1,4-dioxa-7,10,13,16-tetraaza-cyclooctadecane-N,N',N'',N'''-tetrahydrobromide (1.74 g, 3 m-mol) in 40 mL of absolute ethanol (99.9%) mixture. The mixture was stirred at room temperature for 1 hr. The KBr was removed by filtration, and solvents were removed by vacuum distillation. The white residue obtained was dissolved in 20 mL of water.

For the synthesized N-ac$_4$[18]aneN$_4$O$_2$ was dissolved at bromoacetic acid of 2.45 g (17.6 mmol) in 20 mL of ice water (1-2 °C). A solution of 1.7 g of KOH (87%) in 20 mL of water was added dropwise to potassium bromoacetate at 2-5 °C until pH of the solution reached 12.0.

1,4-dioxa-7,10,13,16-tetraazacyclooctadecane and Br-CH_2COOK solution were concent-rated to 10 mL. The rest of the aqueous KOH solution described above was used to maintain the pH of the reaction solution at 11.5-12.0. The reaction solution was kept at 40-42 °C for 5 hr., and then at room temperature for 16 hr. It was neutralized to pH 9.0 with 6 M HCl, and then concentrated to 10 mL.

For the synthesized N-meac$_4$[18]aneN$_4$O$_2$ was dissolved at 2-bromopropionic acid (or bromoacetic aid) of 2.69 g (17.6 mmol) in 20 mL of ice cold water (1-2 °C). A sol-ution of 1.7 g of KOH (87%) in 20 mL of water was added dropwise to potassium 2-bromopropionate (or potassium bromoacetate) at 2-5 °C until pH of the solution reac-hed 12.0.

1,4-dioxa-7,10,13,16-tetraazacyclooctadecane and Br-$(CH_3)CHCH_2COOK$ (or $BrCH_2CH_2COOH$) solution were mixed and warmed up to 40-42 °C. The rest of the aqueous KOH sol-ution described above was applied to maintain the pH range of the reaction solution to 11.5-12.0. The reaction solution was kept at 40-42 °C for 5 hr., and then was concentrated to 10 mL.

The concentrated solutions were loaded on a column of Dowex 1×80-50 ion exchange resin of the OH^- form (15 mm×300 mm) respectively. They were eluted successively with 200 mL of water, 200 mL of 0.01 M HCl, and 300 mL of 0.1 M HCl. The eluate with pH=3.0 contained the pure ligands. After elution with 100 mL of 0.2M HCl, another tetra-HBr salts were obtained.

N-ac$_4$[18]aneN$_4$O$_2$, yield 67%, ^{1}H NMR (D_2O-NaOD, PD=13.2): δ 3.66 (t, 2H, -OCH_2CH_2N-), 3.42 (t, -OCH_2CH_2N-), 3.48 (s, 2H, -NCH_2CH_2N-), 2.60 (t, 2H, -NCH_2COOH), Anal. cacld. for $C_{16}H_{36}O_{10}N_4$: C; 43.20, H; 8.10, N; 12.60. Found: C; 43.15, H; 8.08, N; 12.55.

N-meac$_4$[18]aneN$_4$O$_2$, yield 75%, ^{1}H NMR (D_2O-NaOD, pD=13.2): δ 3.96 (q, 1H, -NCH (CH_3)COOH, 3.60 (t, 2H, -OCH_2CH_2N), 3.40 (t, 2H, -CH_2CH_2N-), 3.48 (s, 2H, -NCH_2CH_2N-), 1.52 (d, 3H, -NCH(CH_3)COOH). Anal Cacld for $C_{16}H_{36}O_{10}N_4$: C; 43.20, H; 8.10, N; 12.60. Found: C; 43.15, H; 8.08, N; 12.55.

Other reagents and standard solution. Transition metal ion (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) solutions were prepared about 0.025 M from the analytical grade of chloride or perchlorate salts with demineralized water, and were standardized by titration with Na_2H_2EDTA. Lanthanide metal ion (Ce^{3+}, Eu^{3+}, Gd^{3+}, and Yb^{3+}) solutions were prepared from the analytical grade of metal oxide with perchloric acid and standardized by titra-tion with Na_2H_2EDTA. A stock solutions of the ligands, N-ac$_4$[18]aneN$_4$O$_2$ and N-meac$_4$[18]-aneN$_4$O$_2$ were prepar-ed with the demineralized water and standardized by co-mplexometric titration with cupric perchlorate.

Potentiometric equipment and calculation of equilibrium constants. Be-ckmann Model φ 71 pH meter (PHC 4400 combined pH electrode) was used for the potentiometric titrations. The determination of protonation constants of the ligands was performed with the ligand of 25 mL solution (2.50×10-3 M), and was measured by titration with the standardized 0.0491 M NaOH solution. The ionic strength was adjusted to 0.1 M $NaClO_4$ solution in the thermostated electrode at 25.0±0.1 oC: The value of Kw=[H+][OH−] used in the computations was 10-13.8018. The protonation constants ($K_i^H = \{[LH_i]\} / \{[LH_{i-1}]][H]_i\}$ were calculated by fitting potentiometric data to the PKAS program.[18] The potentiometric equilibrium measurements were made on 25.00 mL of ligand solution ≅2.50×10^{-3} M diluted to final volume of 62.5 mL, first in the absence of metal ions and then in presence of each metal ion for which the M_L : M_M ratio 1 : 1.

The pH data were titrated with standardized 0.0491 M NaOH solution. The ionic strength adjusted to 0.1 M KCl for N-ac$_4$[18]aneN$_4$O$_2$, and 0.1 M $NaClO_4$ for N-meac$_4$-[18] aneN$_4$O$_2$. The stability constants of various species formed in the aqueous solution were obtained from the experimental data with the aid of the BEST program.[18]

The most of the constants were obtained by competition reactions with EDTA. We obtained the initial computation of the form of over all stability constants(β) values: β= $[M_mL_lH_h]/[M]^m[L]^l[H]^h$. The differences of the various log's provide the step-wise formation and protonation reaction constants.

Results and Discussion

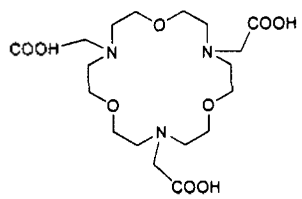
Protonation constants. In the present study KCl or $NaClO_4$ are used as the ionic medium at 0.1 M ionic strength. The values of the protonation constants of N-ac$_4$-[18]aneN$_4$O$_2$ obtained in 0.1 M $NaClO_4$, and those of the N-meac$_4$[18]aneN$_4$O$_2$ determined in 0.1 M KCl can be seen in Table 1 together with the values determinded at the previous work for 1,7,13,-trioxa-4,10,16-triazacyclooctadecane-N,N', N''-triacetic acid, N-ac$_3$[18]aneN$_3$O$_3$ and 1,7,13,-trioxa-4,10, 16-triazacyclooctadecane-N,N',N''-trimethylacetic acid, N-meac$_3$[18]aneN$_3$O$_3$.[10,17]

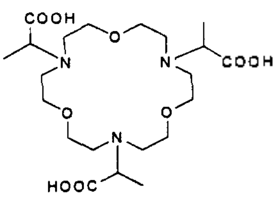
The protonation constants (logK_i^H) of the N-ac$_4$[18]ane-N$_4$O$_2$ were 9.31 for logK_1^H, 8.94 for logK_2^H, 7.82 for logK_3^H,

Table 1. Protonation constants ($\log K_i^H$) of N-ac$_4$[18]aneN$_4$O$_2$ and N-meac$_4$[18]aneN$_4$O$_2$ in aqueous solutions

Equilibrium Quotient	Protonation constant ($\log K_i^H$)			
	N-ac$_4$[18]aneN$_4$O$_2$	N-meac$_4$[18]aneN$_4$O$_2$	N-ac$_3$[18]aneN$_3$O$_3$[a]	N-meac$_3$[18]aneN$_3$O$_3$[b]
	0.1M KCl 25 °C	0.10M NaClO$_4$ 25 °C	0.1M KCl 25 °C	0.10M NaClO$_4$ 25 °C
$\frac{[LH^+]}{[L][H^+]}$	9.31	9.34	9.57	9.70
$\frac{[LH_2^{2+}]}{[LH^+][H^+]}$	8.94	9.13	8.15	9.18
$\frac{[LH_3^{3+}]}{[LH_2^{2+}][H^+]}$	7.82	8.05	7.67	7.27
$\frac{[LH_4^{4+}]}{[LH_3^{3+}][H^+]}$	4.48	5.86	2.05	3.38
$\frac{[LH_5^{5+}]}{[LH_4^{4+}][H^+]}$	2.94	3.55	1.07	2.94

[a]Reference 10. [b]Reference 17.


N-ac$_4$[18]aneN$_4$O$_2$


N-meac$_4$[18]aneN$_4$O$_2$

4.48 for $\log K_4^H$ and 2.94 for $\log K_5^H$. And the proto-nation constants of the N-meac$_4$[18]aneN$_4$O$_2$ were 9.34 for $\log K_1^H$, 9.13 for $\log K_2^H$, 8.05 for $\log K_3^H$, 5.86 for $\log K_4^H$, and 3.55 for $\log K_5^H$. For the 1-oxa-4,7,10-triazacyclodod-ecane-N,N',N''-triacetic acid, N-ac$_3$[12]aneN$_3$O, NMR spectroscopy titration has been known[19] that two higher values of the protonation constants correspond to the proto-nation of nitrogen atoms, but the third and fourth correspond to the protonation of the carboxylate groups. In the ligands, N-ac$_4$[18]aneN$_4$O$_2$ and N-meac$_4$[18]aneN$_4$O$_2$, three hi-gher values of the protonation constants corresponded to the protonation of nitrogen atoms, and the fourth and fifth correspond to the protonation of the carboxylate g-roups.

In the ligands, N-ac$_3$[18]aneN$_3$O$_3$ and N-meac$_3$[18]aneN$_3$O$_3$, the nitrogen atoms are separated by longer chains (-CH$_2$CH$_2$OCH$_2$CH$_2$-) and the ring is less rigid, when compared with the N-ac$_4$[18]aneN$_4$O$_2$ and N-meac$_4$[18]aneN$_4$O$_2$. All the nitrogen atoms are protonated before the carboxylate groups, because the electrostatic repulsions between the positive charges on the nitrogen atoms are weaker than those of the N$_4$O$_2$ macro-cyclic derivative. And the difference between the values of protonation constants of N-ac$_4$[18]aneN$_4$O$_2$ and N-meac$_4$[18]aneN$_4$O$_2$ is regard as the basicities of N atom and steric effect of methyl group.

Stability constants of divalent metal ions. Table 2 and Figure 1 show the stability constants for the complexes of the divalent metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) studied in the present works with N-ac$_4$[18]aneN$_4$O$_2$ and N-meac$_4$[18]aneN$_4$O$_2$.

Table 2. Stability constants ($\log K_{ML}$) for metal complexes of macrocyclic ligands with several divalent metal ions

Cation	Quotient	Stability constant ($\log K_{ML}$)			
		N-ac$_4$[18]aneN$_4$O$_2$	N-meac$_4$[18]aneN$_4$O$_2$	N-ac$_3$[18]aneN$_3$O$_3$	N-meac$_3$[18]aneN$_3$O$_3$
		0.1M KCl, 25 °C	0.1M NaClO$_4$, 25 °C	0.1M KCl, 25 °C	0.1M NaClO$_4$, 25 °C
Co^{2+}	[ML]/[M][L]	12.52	16.00	9.33	10.89
Ni^{2+}	[ML]/[M][L]	13.50	16.50	9.84	10.68
Cu^{2+}	[ML]/[M][L]	14.62	17.30	14.88	13.45
Zn^{2+}	[ML]/[M][L]	13.00	14.53	9.89	13.00

In this table, the known values[10,17] for the same set of metal ions with ligands N-ac$_3$[18]aneN$_3$O$_3$ and N-meac$_3$[18]aneN$_3$O$_3$ are also listed for comparison. The ligands may form several complexes species, according to the constants calculated by the BEST program[18]: all of them form ML (M is metal, and L is ligand), some of them form protonated and hydroxo complex species. For all the ML complexes formed with divalent metal ions, the stability constants, $\log K_{ML}$ for the complexes of divalent transition metal ions with N-ac$_4$[18]aneN$_4$O$_2$ were 12.52 for Co^{2+}, 13.50 for Ni^{2+}, 14.62 for Cu^{2+}, and 13.00 for Zn^{2+}. And stability constants of N-meac$_4$[18]aneN$_4$O$_2$ with transition metal ions were 16.00 for Co^{2+}, 16.50 for Ni^{2+}, 17.30 for Cu^{2+}, and 14.53 for Zn^{2+}. The values of stability constants for the complexes of divalent transition metal ions with N-ac$_4$[18]aneN$_4$O$_2$ or N-meac$_4$[18]aneN$_4$O$_2$ increase more highly than those of N-ac$_3$[18]aneN$_3$O$_3$ or N-meac$_3$[18]aneN$_3$O$_3$. The trend presented by this ligand is probably the result of tredency to form octahedral complexes with the four nitrogen atoms of the ring occupying facial sites with very efficient packing around small metal ions. The higher basicities of the N$_4$O$_2$ ligand are manifested in higher affinity for hydrogen ions.

Another effect that can be observed in the trend shown in Figure 1 is the Irving-Williams order of stability. The high value of Cu^{2+} is due to the special stabilization energy of its hexacoordinate complex by Jahn-Teller distortion.[20]

Stability constants of trivalent metal ions. The stability constants of complexes formed by N-ac$_4$[18]aneN$_4$O$_2$ with Ce^{3+}, Eu^{3+}, Gd^{3+}, and Yb^{3+} have been determined in 0.1 M

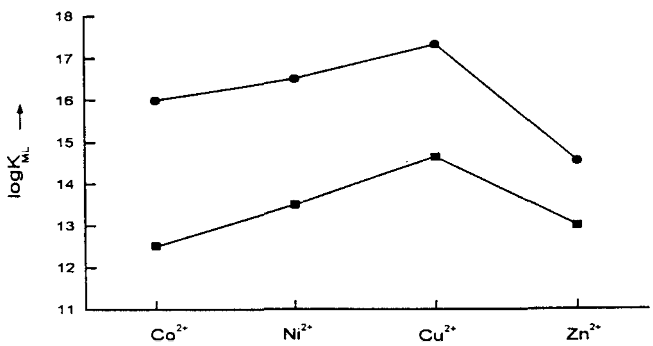


Figure 1. Variation of stability constants ($\log K_{ML}$) of the ligand complexes with several divalent metal ions. ■ : N-ac$_4$[18]aneN$_4$O$_2$, ● : N-meac$_4$[18]aneN$_4$O$_2$.

Table 3. Stability constants (logK_{ML}) for metal complexes of macrocyclic ligands with several trivalent lanthanide metal ions

Cation	Quotient	Stability constant (logK_{ML})	
		N-ac$_4$[18]aneN$_4$O$_2$	N-meac$_4$[18]aneN$_4$O$_2$
		0.01M KCl, 25 °C	0.01M NaClO$_4$, 25 °C
Ce^{3+}	[ML]/[M][L]	15.06	16.00
Eu^{3+}	[ML]/[M][L]	16.00	17.60
Gd^{3+}	[ML]/[M][L]	16.00	17.40
Yb^{3+}	[ML]/[M][L]	17.01	19.12

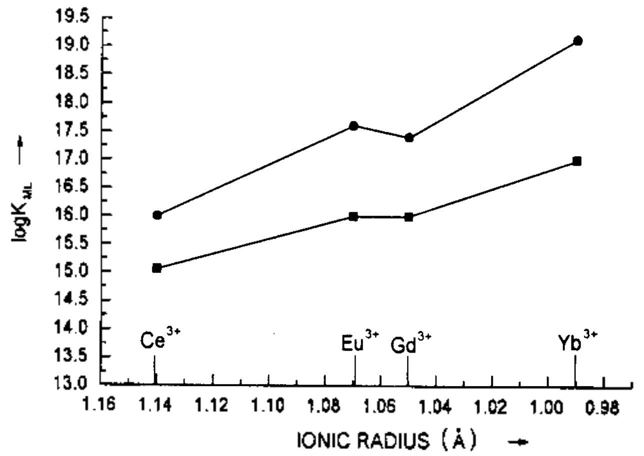


Figure 2. Variation of stability constants (logK_{ML}) of the ligand complexes with several trivalent metal ions. ■ : N-ac$_4$[18]aneN$_4$O$_2$ ● : N-meac$_4$[18]aneN$_4$O$_2$.

KCl ionic medium at 25 °C, and the stability constants of complexes formed by and N-meac$_4$[18]aneN$_4$O$_2$ with trivalent metal ions have been determined in 0.1 M $NaClO_4$ ionic medium at 25 °C. The obtained values can be seen in Table 3 and Figure 2, together with the values determined in the previous work for N-meac$_3$[18]aneN$_3$O$_3$. The logarithm stability constants, logK_{ML} of the complexes formed by N-ac$_4$-[18]aneN$_4$O$_2$ with trivalent metal ions have been determined as 15.06 for Ce^{3+}, 16.00 for Eu^{3+}, and Gd^{3+}, 17.01 for Yb^{3+}, and those of the complexes formed by N-meac$_4$[18]aneN$_4$O$_2$ with Ce^{3+}, Eu^{3+}, Gd^{3+}, and Yb^{3+} have been determined as 16.00 for Ce^{3+}, 17.06 for Eu^{3+}, 17.40 for Gd^{3+}, and 19.12 for Yb^{3+}. The values of the stability constants on trivalent metal ions with those ligands are increasing according to the increase of atomic number, due to increase of acidity. But the value of stability constant of Gd^{3+} ion is less than that of Eu^{3+} ion. This disorder behavior is also reported by Moeller.[21] The stability constants of N-ac$_4$[18]aneN$_4$O$_2$ with trivalent metal ions are lower than those of N-meac$_4$-[18]aneN$_4$O$_2$. This means that geometric configuration of ligand leads to a ligand which cannot place all the donor atoms in position for coordination, due to the higher basicities of N-meac$_4$[18]aneN$_4$O$_2$.

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