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Stability Studies of Divalent and Trivalent Metal Complexes with 1,7,13-Trioxa-4,10,16-triazacyclooctadecane-N,N',N''-tri(methylacetic acid)

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The potentiometric methods have been used to determined the protonation constants ($\log K_i^H$) for the synthesized 1,7,13-trioxa-4,10,16-triazacyclooctadecane-N,N',N''-tri(methylacetic acid) [N_3O_3 -tri(methylacetic acid)] and the stability constants ($\log K_{ML}$) of the complexes of divalent and trivalent metal ions with the ligand N_3O_3 -tri(methylacetic acid). The protonation constants of N_3O_3 -tri(methylacetic acid) were 9.70 for $\log K_1^H$, 9.18 for $\log K_2^H$, 7.27 for $\log K_3^H$, 3.38 for $\log K_4^H$, and 2.94 for $\log K_5^H$. The stability constants for the complexes of divalent metal ions with N_3O_3 -tri(methylacetic acid) were 10.39 for Co^{2+} , 10.68 for Ni^{2+} , 13.45 for Cu^{2+} , and 13.00 for Zn^{2+} . The order of the stability constants for the complexes of the divalent metal ions with N_3O_3 -tri(methylacetic acid) was $Co^{2+} < Ni^{2+} < Zn^{2+} < Cu^{2+}$. The stability constants for the complexes of trivalent metal ions with N_3O_3 -tri(methylacetic acid) were 16.20 for Ce^{3+} , 16.40 for Eu^{3+} , 16.27 for Gd^{3+} , and 15.80 for Yb^{3+} . The results obtained in this study were compared to those obtained for similar ligands, 1,7-dioxa-4,10,13-triazacyclooctadecane-N,N',N''-tri(methylacetic acid) and 1,7,13-trioxa-4,10,16-triazacyclooctadecane-N,N',N''-triacetic acid, which have been previously reported.

Introduction

The first macrocyclic compounds containing polyether were reported by Luttingerhaus and Ziefler in 1973.¹ These macrocyclic compounds showed remarkable selectivities toward certain metal ions for the complex formation, and then such ligands can be used in the fields of biochemistry, hydrometallurgy and waste treatment.²⁻⁷

The objective of their research was to determine the stability constants of complexes of some divalent and trivalent metal ions with the macrocyclic ligand having methylacetate groups as N-pendant arms. The stability constants of the metal ions with macrocyclic ligands were determined by various methods. Delgado *et al.*⁸ determined the stability constants of the complexes of some divalent and trivalent metal ions with a series of macrocyclic ligands having acetate groups as N-pendant arms. These series of ligands provided an opportunity to study on the influence of the steric effect of the macrocyclic ring and increasing number of

donor atoms on the stability and selectivity of metal complexes. The metal ions studied include the divalent metal ions, such as Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ca^{2+} , and Pb^{2+} , and trivalent metal ions such as Al^{3+} , Ga^{3+} , Fe^{3+} , In^{3+} , and Gd^{3+} . The series of ligands, which are N,N',N''-triazacycliononane triacetic acid [N_3 -triacetic acid],⁹ 1-oxa-4,7,10-triazacyclododecane-N,N',N''-triacetic acid [N_3O -triacetic acid],¹⁰ and 1,7-dioxa-4,10,13-triazacyclooctadecane-tri(methylacetic acid) [N_3O_2 -tri(methylacetic acid)],¹¹ also provided an opportunity to compare the affinities to the metal ions.

In this work, the protonation constants of the synthesized 1,7,13-trioxa-4,10,16-triazacyclooctadecane-N,N',N''-tri(methylacetic acid) [N_3O_3 -tri(methylacetic acid)] and the stability constants of the complexes of some divalent transition metal ion (Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) and trivalent lanthanide metal ions (Ce^{3+} , Eu^{3+} , Yb^{3+} and Gd^{3+}) with this macrocyclic ligand were determined. The ligands of N_3O_2 -tri(methylacetic acid) and N_3O_3 -triacetic acid have been studied previously.^{8,11} The results obtained in this experiments

were compared to the data of N_3O_2 -tri(methylacetic acid)¹¹ and N_3O_3 -triacetic acid.⁸

Experimental

Materials and standard solutions. 2-Bromopropionic acid, toluenesulfonyl chloride, 2-(2-aminoethoxy) ethanol, 2-(2-chloroethoxy)ethanol, phosphorous tribromide, Dowex 1×8-50 ion exchange resin and silica gel (200-400 mesh, 60 Å) were obtained from Aldrich Chemical Co. They were used without further purification. Dowex 1×8-50 resin was treated with 2 M KOH aqueous solution to convert its surface to the OH^- form. Transition metal ion (Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+}) solutions about 0.025 M were prepared from the analytical grade of chloride or perchlorate salts with the demineralized water and standardized by titration with Na_2H_2EDTA (disodium salt of ethylenediamine tetraacetic acid).¹² Lanthanide metal ion (Ce^{2+} , Eu^{2+} , Gd^{2+} and Yb^{2+}) solutions were prepared from the analytical grade of metal oxide with perchloric acid and standardized by titration with Na_2H_2EDTA . A stock solution of the ligand, N_3O_3 -tri(methylacetic acid), was prepared with the demineralized water and standardized by complexometric titration with cupric perchlorate.

Synthesis of N_3O_3 -tri(methylacetic acid). 1,7,13-trioxo-4,10,16-triazacyclooctadecane trihydrobromide was prepared by previously reported procedures.¹³⁻¹⁵ N_3O_3 -tri(methylacetic acid) was prepared by improved procedure from previously reported one.¹⁶ The synthetic route of the azacrown compound, N_3O_3 -tri(methylacetic acid) was shown in Scheme 1.

Ground KOH (87%) pellets, 0.77 g (12 mmol) were added to suspension of 1,7,13-trioxo-4,10,16-triazacyclooctadecane trihydrobromide, 1.008 g (2 mmol) in 40 mL of absolute ethanol (99.9%). The mixture was stirred at room temperature for 1 hr. The KBr was removed by filtration, and solvent was removed by vacuum distillation. The white residue obtained was dissolved in water, 20 mL. 2-Bromopropionic acid, 2.02 g (13.2 mmol) was dissolved in ice water, 20 mL. A solution of KOH (87%), 1.7 g in water of 20 mL, was added dropwise to potassium 2-bromopropionic acid at 2-5 °C until pH of the solution reaches 12.0. 1,7,13-trioxo-4,10,16-triazacyclooctadecane and $Br(CH_2)_2CHCOOK$ solution were mixed and warmed up to 40-42 °C. The rest of aqueous KOH solution described above was applied to maintain the pH range of the reaction solutions 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 resulting solution was loaded on a column of Dowex 1×8-50 ion exchange resin of the OH^- form (15×300 mm). It was eluted successively with 200 mL water, 0.01 M HCl of 200 mL, and 0.1 M HCl of 300 mL. The eluate with pH=3.0 solution contained the pure ligand. After elution with 100 mL of 0.2 M HCl,

tri-HBr salt was obtained: total yield 62%; ¹H NMR (D_2O -NaOD, pD 13.0): 3.48 (t, 14H, $-CH_2OCH_2-$), 3.22 (s, 3H, $-CHCOO-$), 2.85 (t, 10H, $-CH_2NCH_2-$), 2.41-2.63 (t, 9H, $-CH_3$); Anal. Calcd for $C_{21}H_{36}N_3O_9 \cdot 3NaCl$: C, 39.03; H, 5.61; N, 6.50. Found: C, 39.23; H, 5.28; N, 6.24.

Potentiometric equipment and measurements.

Beckmann Model ϕ 71 pH meter (PHC 4400 combined pH electrode) was used for the potentiometric titrations. The determinations of protonation constants of the ligand were made on the ligand of 25 mL solution (2.50×10^{-3} M), and were measured by titrating with using the standardized 0.0491 M NaOH solution. The ionic strength adjusted to 0.10 M $NaClO_4$ solution in the thermostated electrode at 25.0 ± 0.1 °C. The protonation constants, $K_i^H = [LH_i]/[LH_{i-1}][H^+]$ were calculated by fitting the potentiometric data using the PKAS program.¹⁷ The value of $K_w = [H^+][OH^-]$ used in the computations was $10^{-13.80}$.¹⁷

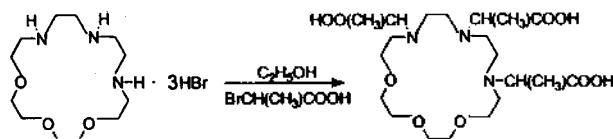
The potentiometric equilibrium measurements were made on 25.00 mL of the ligand solutions $\approx 2.50 \times 10^{-3}$ M diluted to a final volume of 62.50 mL, first in the absence of metal ions and then in presence of each metal ion for which the $m_L : m_M$ ratios 1 : 1. The pH data were titrated with standardized 0.0491 M NaOH solution. The ionic strength adjusted to 0.10 M $NaClO_4$ aqueous solution. The stability constants of various species formed in the aqueous solution were obtained from the experimental data with the aid of the BEST program.¹⁷ Most of the constants were obtained by competition reactions with EDTA. We obtained in the initial computation the form of over all stability constants (β) values: $\beta = [M_m L_n H_i] / [M]^m [L]^n [H]^i$. The differences of the various $\log \beta$'s provide the stepwise formation and protonation reaction constants.

Results and Discussion

Protonation constants. The stepwise protonation constants of N_3O_3 -tri(methyl-acetic acid) determined at 25 °C in 0.1 M $NaClO_4$ were summarized in Table 1, together with values for N_3O_2 -tri(methylacetic acid) and N_3O_3 -triacetic acid taken from the literature.^{8,11} The protonation constants ($\log K_i^H$) of the N_3O_3 -tri(methylacetic acid) were 9.70 for $\log K_1^H$, 9.18 for $\log K_2^H$, 7.27 for $\log K_3^H$, 3.38 for $\log K_4^H$, and 2.94 for $\log K_5^H$. The protonation of all nitrogen atoms occurs before that of carboxylate groups, which was inferred from ¹H NMR titration.¹⁴

For the 15-membered macrocycle, Amorim *et al.*¹⁹ reported that NMR spectroscopy titration had been shown that first two higher values of the protonation constants were corresponded to the protonation of nitrogen atoms, but the third and fourth were corresponded to the protonation of the carboxylate groups. In the 18-membered macrocycle, the nitrogen atoms are separated by longer chains ($-CH_2CH_2OCH_2CH_2-$) and the ring is less rigid because of the larger size of the cavity of this ligand. The greater flexibility of ring can minimize the repulsion of proton. Therefore, the first three protonation constants of the 18-membered macrocycle correspond to the protonation of the adjacent nitrogen atoms.

The values of the protonation constants for N_3O_3 -tri(methylacetic acid) are similar to those found for N_3O_3 -triacetic acid, as the protonations occur on nitrogen atoms



Scheme 1. Synthetic route of N_3O_3 -tri(methylacetic acid).

Table 1. Protonation constants ($\log K_i^H$) of N_3O_3 -triacetic acid, N_3O_2 -tri(methylacetic acid) and N_3O_3 -tri(methylacetic acid) in aqueous solution

Equilibrium quotient	Protonation constant ($\log K_i^H$)		
	N_3O_2 -tri(methylacetic acid) ^a	N_3O_3 -triacetic acid ^b	N_3O_3 -tri(methylacetic acid)
	0.1 M NaClO ₄ 25 °C	0.1 M KCl 25 °C	0.1 M NaClO ₄ 25 °C
$\frac{[LH^+]}{[L][H^+]}$	8.10	9.57	9.70
$\frac{[LH_2^{2+}]}{[LH^+][H^+]}$	7.48	8.15	9.18
$\frac{[LH_3^{3+}]}{[LH_2^{2+}][H^+]}$	4.97	7.67	7.27
$\frac{[LH_4^{4+}]}{[LH_3^{3+}][H^+]}$	4.70	2.05	3.38
$\frac{[LH_5^{5+}]}{[LH_4^{4+}][H^+]}$		1.07	2.94

^a Reference 11. ^b Reference 8.

separated by long chain ($-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$). However, $\log K_3^H$ of N_3O_2 -tri(methyl-acetic acid) is lower than those of N_3O_3 -triacetic acid and N_3O_3 -tri(methylacetic acid) since the third nitrogen of N_3O_2 -tri(methylacetic acid) is separated by an ethylene group from the other protonated nitrogen. The differences between the protonation constants of N_3O_3 -triacetic acid and N_3O_3 -tri(methylacetic acid) is regarded as strain effect of methyl group.

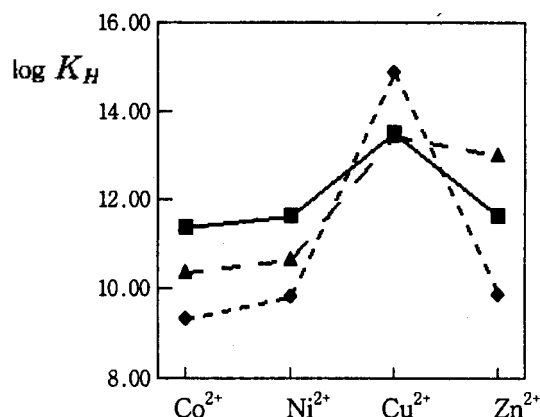
Stability constants of divalent metal ions. Table 2 and Figure 1 exhibit the stability constants for the divalent metal ions studied in the present work (Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) with N_3O_3 -tri(methylacetic acid).

In Table 2, the published values for the same set of metal ions with ligands N_3O_3 -triacetic acid and N_3O_2 -tri(methylacetic acid) are also shown for comparison. The ligands will form several complex species, according to constant calculated by the BEST program¹⁷: all of them form ML (M is metal, and L is ligand), some of them form protonated and hydroxo complex species, but the most of them form binuclear species. For all ML complexes formed with

Table 2. Stability constants for the metal complexes of macrocyclic ligand with several divalent transition metal ions

Cation	Quotient	Stability constant ($\log K_{ML}$)		
		N_3O_2 -tri(methylacetic acid) ^a	N_3O_3 -triacetic acid ^b	N_3O_3 -tri(methylacetic acid)
		0.1 M NaClO ₄ 25 °C	0.1 M KCl 25 °C	0.1 M NaClO ₄ 25 °C
Co^{2+}	$[\text{ML}]/[\text{M}][\text{L}]$	11.40	9.33	10.89
Ni^{2+}	$[\text{ML}]/[\text{M}][\text{L}]$	11.63	9.84	10.68
Cu^{2+}	$[\text{ML}]/[\text{M}][\text{L}]$	13.51	14.88	13.45
Zn^{2+}	$[\text{ML}]/[\text{M}][\text{L}]$	11.65	9.89	13.00

^a Reference 11. ^b Reference 8.

**Figure 1.** Variation of the stability constants, $\log K_{ML}$ for the metal complexes N_3O_3 -triacetic acid, N_3O_2 -tri(methylacetic acid), N_3O_3 -triacetic acid, and N_3O_3 -tri(methylacetic acid) with divalent transition metal ions. ■: N_3O_2 -tri(methylacetic acid), ◆: N_3O_3 -triacetic acid, ▲: N_3O_3 -tri(methylacetic acid)

divalent metal ions the values of stability constants decrease with increase of ring size, in spite of the increase of the potential number of oxygen donor atoms and overall basicity.

The logarithm stability constants, $\log K_{ML}$ for the complexes of divalent transition metal ions with N_3O_3 -tri(methylacetic acid) were 10.39 for Co^{2+} , 10.68 for Ni^{2+} , 13.45 for Cu^{2+} , 13.00 for Zn^{2+} . Generally, the order of the stability constants for divalent metal ions with most of ligand was reported with $\text{Co}^{2+} < \text{Ni}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+}$ by Irving-Williams series. As shown in Figure 1, it agree with the stability order of Irving-Williams series for N_3O_3 -tri(methylacetic acid). The high value of Cu^{2+} is due the special stabilization energy of its hexacoordinate complex by Jahn-Teller distortion.¹⁹

The stability constants of N_3O_3 -tri(methylacetic acid) with divalent metal ions are lower than those of N_3O_2 -tri(methylacetic acid). The tendency to form protonated complexes increase with the size of the ring for the same metal ion but the increase is less for the larger metal ions. The higher basicities of the larger ligand is manifest in the higher affinity for hydrogen ions.⁸ The stability constants of N_3O_3 -tri(methylacetic acid) with divalent metal ions are larger than those of N_3O_3 -triacetic acid. They are on account of geometric configuration and first protonation constant of ligand.

These more covalently bonding metal ions with ligands could have stricter stereochemical demands for specific geometries, and thus the adjustment of the ligand to the metal ion is more difficult from the result that probably some of the donor atoms are not involved in the coordination to the metal ion. 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, enthalpic and entropic variations, and some X-ray structures would be necessary to provide further insights.

Stability constants of trivalent metal ions. The stability constants of complexes formed by N_3O_3 -tri(methylacetic acid) with Ce^{3+} , Eu^{3+} , Gd^{3+} and Yb^{3+} have been determined in 0.1 M NaClO₄ ionic medium at 25.0 °C. The values obtained can be seen in Table 3 and Figure

Table 3. Stability constants for the metal complexes of N_3O_3 -tri(methylacetic acid) N_3O_2 -tri(methylacetic acid) with several trivalent Lanthanide metal ions ($\mu=0.10$ M KCl, $t=25$ °C)

Cation	Stability constant ($\log K_{ML}$)	
	N_3O_2 -tri(methylacetic acid) ^a	N_3O_3 -tri(methylacetic acid)
Ce ³⁺	11.26	16.20
Eu ³⁺	11.55	16.42
Gd ³⁺	11.49	16.27
Yb ³⁺	11.80	15.80

^aReference 11.

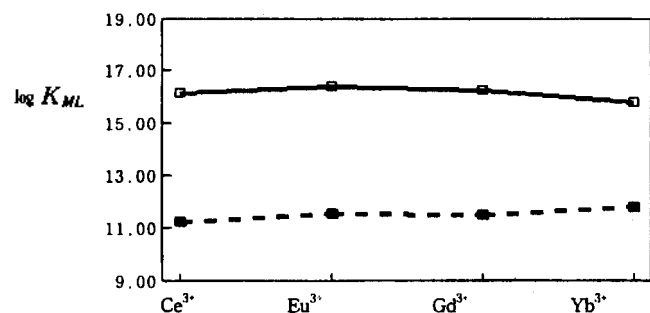


Figure 2. Variation of the stability constants ($\log K_{ML}$) for the metal complexes N_3O_2 -tri(methylacetic acid) and N_3O_3 -tri(methylacetic acid) with trivalent lanthanide ions. ■: N_3O_2 -tri(methylacetic acid), □: N_3O_3 -tri(methylacetic acid)

2, together with the values determined in the previous work for N_3O_2 -tri(methylacetic acid).¹¹

The logarithm stability constants, $\log K_{ML}$, of the complexes formed by N_3O_3 -tri(methylacetic acid) with Ce³⁺, Eu³⁺, Gd³⁺ and Yb³⁺ have been determined on 16.20 for Ce³⁺, 16.42 for Eu³⁺, 16.27 for Gd³⁺ and 15.80 for Yb³⁺. Generally the values of the stability constants for trivalent metal ions with the ligand are increasing according to increase of atomic number, due to increase of acidity. But the values of stability constant of Gd³⁺ and Yb³⁺ ions are less than that of Eu³⁺ ion. The disorder behavior of Gd³⁺ is reported by Moeller.²⁰ For the disorder behavior of Yb³⁺ the values of stability constants do not provide enough information, therefore the complexes of Yb³⁺, would be necessary to provide further insights.

The stability constants of N_3O_3 -tri(methylacetic acid) with trivalent metal ions are larger than those of N_3O_2 -tri(methylacetic acid). This means that decrease of the ring size leads to a ligand which cannot place all the donor atoms in the position for coordination, but the larger ligands which are more flexible seem to adapt better to the size of

the metal ions and to bring the donor atoms near to the metal ions.

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