

Synthesis of Chelating Agents. XII.¹⁾ Chelating Behavior of 3,3-Dimethylbutane-1,2-diamine-*N,N,N',N'*-tetraacetic Acid with Some Alkaline Earth Metals*

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Synopsis. The chelate stability constants of 3,3-dimethylbutane-1,2-diamine-*N,N,N',N'*-tetraacetic acid with some alkaline earth metal ions were determined at 25.0 °C and at an ionic strength of 0.10 with KNO₃ as supporting electrolyte by a potentiometric method.

Synthesis and acid dissociation study of 3,3-dimethylbutane-1,2-diamine-*N,N,N',N'*-tetraacetic acid (BEDTA) was previously reported.²⁾ This note is to report on the chelating behavior of the above ligand with alkaline earth metal ions.

Experimental and Calculation

Potentiometric measurements were carried out at 25.0 ± 0.1 °C in aqueous solutions and at an ionic strength of 0.10

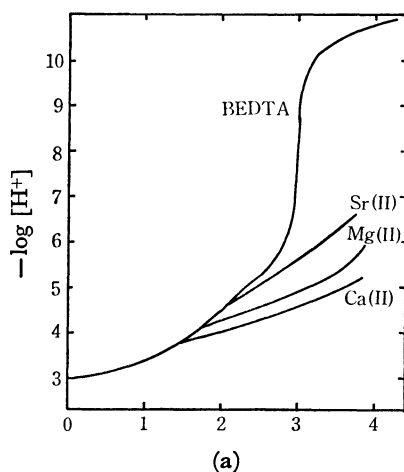


Fig. 1. Potentiometric titration curves of the alkaline earth metal chelates at 25.0 °C in 0.10 M KNO₃ solution, where the mole ratio of a metal ion to the ligand is 1:1 and the concentration of BEDTA 10⁻³ M.

TABLE 1. STABILITY CONSTANTS OF BEDTA AND RELATED LIGANDS WITH SOME ALKALINE EARTH METALS

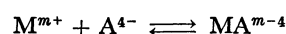
Compound	log <i>K</i> _{MA}		
	Mg(II)	Ca(II)	Sr(II)
BEDTA	11.0	11.8	9.4
EDTA ^{a)}	8.69	10.70	8.63
PDTA ^{a)}	10.29	11.47	9.61
<i>dl</i> -BDTA ^{b)}	11.33	11.49	10.10

a) PDTA: Propane-1,2-diaminetetraacetic acid

b) *dl*-BDTA: *dl*-Butane-2,3-diaminetetraacetic acid

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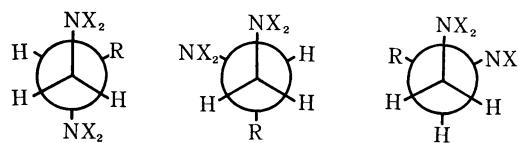
with KNO₃ as supporting electrolyte. Apparatus and procedures were the same as described previously.¹⁾ A solution of the ligand (10⁻³ M, 100 ml) was titrated with 0.1 N KOH solution free from carbonate ion in the presence of an equimolar amount of an alkaline earth metal ion. The titration curves obtained were shown in Fig. 1. Since BEDTA forms exclusively a 1:1 chelate with a multivalent metal ion,



the stability constant $K_{MA} (= [MA^{m-4}] / [M^{m+}][A^{4-}])$ was calculated according to the Bjerrum's standard method.³⁾

Results and Discussion

Stability constants of BEDTA chelates with alkaline earth metal ions are summarized in Table 1 along with those of some methylated homologues of EDTA. One can readily notice that BEDTA is one of the complexane ligands that give the most stable chelates with alkaline earth metal ions. Among them, calcium(II) ion forms the most stable chelate, and magnesium(II) and strontium(II) afford decreasingly less stable ones. Though this stability order is the same as generally observed in complexane ligands, it is noted that the difference between the stabilities of the calcium(II) and magnesium(II) chelates is relatively small as compared with those of the other EDTA homologues.



(I) PDTA: X=CH₂COO⁻, R=methyl
 (II) BEDTA: X=CH₂COO⁻, R=*t*-butyl
 (III) BEDA: X=H, R=*t*-butyl

Upon chelate formation with a metal ion, the BEDTA tetraanion moiety would take the *syn*-conformation of II preferably to III since the latter, though being also of a *syn*-conformation, would be subject to considerable steric hindrance between *t*-butyl group and the resulting out-of-plane (R) glycinate ring.⁴⁾ A study on the rotational isomerism of propane-1,2-diaminetetraacetic acid (PDTA) in a solution showed that among the conformations of the free tetraanion, I, II, and III, the latter two were present to an equal extent.⁵⁾ Increased size of the alkyl substituent in BEDTA, however, would favor to the less congested conformation II and, therefore, presumably causes the increase in the fraction of II, while decreases that of III.

The precursory diamine, 3,3-dimethyl-1,2-diaminobutane (BEDA), was found to form also very stable

complexes as compared with those of homologous 1,2-diamines. This behavior upon chelate formation was also ascribed to the bulkiness of *t*-butyl group which restricted the internal rotation in the free ligand molecule to fix the two amino group in a *syn-clinal* position II favorable to chelate ring formation.⁶⁾ Although no direct evidence was obtained, the behavior of the precursory diamine and the molecular model study of BEDTA indicated the predominance of the conformer II in the free tetraanion of BEDTA.

Thus an entropy contribution due to the steric effect, as well as an enthalpy contribution due to the electron-releasing effect of *t*-butyl group, would be responsible for the high stability of the present complexane ligand.

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