The Chelating Behavior of β-Aminoethylmercaptan with Alkaline Earth Metals[*1]

By Yuichi TSUCHITANI,[*2] Takeshi ANDO and Keihei UENO

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During the course of our investigation into the syntheses of new chelating agents, an intermediate product, β-aminoethylmercaptan (hereafter referred to as AEM), drew our attention as a masking agent in the chelatometric titration.[1] This investigation also made it necessary that we get basic information on the chelating behavior of this bidentate ligand with various metal ions.

Many papers have been published on the chelate-forming properties of AEM in solid[2,3], as well as in solution states;[4-7] the reported data on the chelate stability constant include data on such metal ions as cadmium(II), cobalt(II), nickel(II), lead(II) and zinc(II).[8] However, no information is available on its chelating behavior with alkaline earth metals. This paper will report the results of the chelate stability measurement of AEM with alkaline earth metals.

Experimental

Reagents. — AEM which had been obtained as hydrochloride from the Evans Chemitics, Inc., New York, was recrystallized repeatedly from ethanol in a nitrogen atmosphere. The material was very hygroscopic and had to be stored in nitrogen over phosphorus pentaoxide. It melted at 70∼70.5°C in a sealed tube (reported m. p. 70.2∼70.7°C[9]).

Found: C, 20.81; H, 6.90%. Calcd. for $C_2H_7NS\cdot HCl$: C, 21.13; H, 7.10%.

The purity of the material was also checked by the iodometry of the -SH group; it was found to be 99.37±0.40%. The strength of the aqueous solution of the reagent decreased by 0.5∼1.0% over a 3-day period even when it was kept in nitrogen in a refrigerator; therefore, the exact strength of the solution was estimated by taking the mean value of the strengths before and after measurement.

All the metal ions used in this study were in nitrate form; the concentration of their solutions was determined by the EDTA titration.

The Measurement of the Dissociation and the Chelate Stability Constants. — The experimental method consisted of the potentiometric titration of the ligand in the absence and in the presence of

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[*1] Contribution No. 44 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University.

[*2] Present address: Central Research Laboratory, Ajinomoto Co., Kawasaki.

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the metal ions, using a 0.10 N sodium hydroxide solution as the titrant. The ionic strength was kept constant at $\mu=0.10$ with potassium nitrate, while the concentrations of the ligand and the metal ions were kept at $1\sim2\times10^{-3}$ M. Titrations were carried out with solutions with 1 : 1 and 1 : 2 metal ligand ratios at 25±0.1°C in a current of nitrogen in the absence of atmospheric and dissolved oxygen.

The hydrogen ion concentration was measured by means of a Hitachi Horiba Model P pH-meter with a glass and a calomel electrode. A fluctuation in the pH value was seen when a fresh glass electrode was used; only reproducible readings were taken as the titration data.

Results and Discussion

The acid dissociation constant of the ligand was calculated, according to Bjerrum's method, from the titration curve of the ligand in the absence of metal ions (Fig. 1). The equilibria and the dissociation constants to be determined are expressed as:

$$H_2A^+ \rightleftharpoons H^+ + HA\,;\ k_1=(H^+)(HA)/(H_2A^+)$$

$$HA \rightleftharpoons H^+ + A^-\,;\ k_2=(H^+)(A^-)/(HA)$$

where H_2A^+ represents the protonated ligand ($HSCH_2CH_2N^+H_3$). The values of pk_1 and pk_2 were obtained from Bjerrum's formation curve, and their accuracies were checked by the successive approximation method of Carlson, McReynolds and Verhoek.10) As Table I shows, these values agree fairly well with the reported values when the differences in experimental conditions are taken into account.

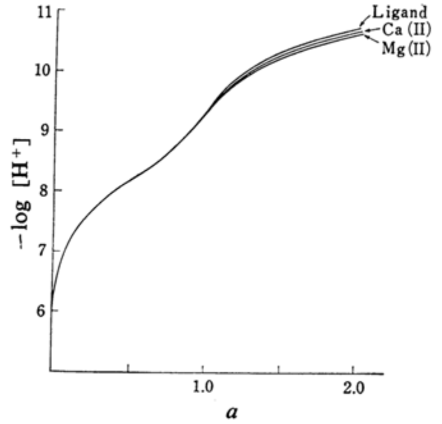

Fig. 1. Titration curves of AEM with and without the metal ions.
$t=25$°C; $\mu=0.10$ (KNO_3); Concentration of ligand, about 1×10^{-3}

The titration curves of the solutions with a 1 : 1 metal to ligand ratio for calcium(II) and magnesium(II) are shown in Fig. 1. Although the titration of solutions with a 1 : 2 ratio was also carried out, no indication of the formation of a 1 : 2 chelate was found. The chelate stability constant for the 1 : 1 may be defined as follows:

$$M^{2+} + A^- \rightleftharpoons MA^+\,;$$

$$K_{MA}=(MA^+)/(M^{2+})(A^-)$$

where M^{2+} and A^- represent alkaline earth metal ions and the deprotonated ligand $H_2NCH_2CH_2S^-$ respectively. The chelate stability constants for alkaline earth metals were calculated from these titration curves according to the method developed by Chaberek and Martell.11) When the data obtained from the titration curves in a range of $a=1.4\sim1.7$ were employed, the agreement of the calculated values on each metal ion were not satisfactory. Therefore, fairly consistent values from the narrower range of $a=1.48\sim1.57$ were taken as the chelate stability constants. The main reasons for such a deviation may be an error

TALE I. ACID DISSOCIATION CONSTANTS AND CHELATE STABILITY CONSTANTS OF AEM AND SOME RELATED COMPOUNDS

Ligand	pk_1	pk_2	log K_{MA} for			
			Ba	Ca	Mg	Sr
β-Aminoethylmercaptan						
25°C, $\mu=0.10$	8.19	10.73	1.37	2.21	2.30	1.55
25°C, $\mu=0.15$	8.35	10.81				
Iminodiacetic acid						
20°C, $\mu=0.10$	2.98	9.89	1.67	2.59	2.94	—
Glycine						
20°C, $\mu=0.2$	2.35	—	0.77	1.38	3.44	—
Glycolic acid						
20°C, $\mu=0.2$	3.71	—	0.66	1.11	0.92	0.80

All data except those of the first line are taken form Ref. 8.

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in pH measurement, an error which would increase with decreasing chelate stability, and the decomposition of ligands in the alkaline region. As is shown in Table I, the chelate stability constants for alkaline earth metals are not very high, but they are still appreciable. These values are comparable to those of iminodiacetic acid and are somewhat higher than those of glycolic acid and glycine. The same order of increasing stability, barium< calcium<magnesium, is observed for AEM, glycine and iminodiacetic acid, all of which have nitrogen as one of the donor atoms. These findings suggest that the coordination of nitrogen in AEM is effective, even in the case of alkaline earth metals. In the chelate stability investigation into the marcaptoethyl derivative of iminodiacetic acid,[12] it has been found that the coordination of the $-S^-$ group contributes very little to the chelate stability in the case of alkaline earth metals. Therefore, it is very likely that the chelate formation of AEM with alkaline earth metals takes place mainly through the coordination of the amino nitrogen of the ligand.

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Department of Organic Synthesis
Faculty of Engineering
Kyushu University
Hakozaki, Fukuoka

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