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Polarographic Study of the Cadmium(II)-Ethylenediaminetetrapropionate Chelate

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The d.c. polarographic behavior of the cadmium(II) ion in ethylenediaminetetrapropionate (EDTP) was studied in the pH range from 8.30 to 10.30. Over the entire range of experimental conditions employed, the cadmium(II)ion invariably gave a single well-defined wave corresponding to the following reversible two-electron reduction:

$$\begin{array}{l} \mathrm{CdZ^{2-}} + n\mathrm{H^+} + \mathrm{Hg} + 2\mathrm{e^-} \rightleftharpoons \mathrm{Cd(Hg)} + \mathrm{H}_n\mathrm{Z}^{n-4} \\ \quad\upharpoonleft\downharpoonright \\ \mathrm{CdZ_2{}^{6-}} \end{array}$$

Even in the presence of ammonia or the alaninate ion, the cadmium(II) ion in the EDTP solution also behaves reversibly in a polarographic electrolysis. However, the half-wave potential was found to be shifted to the more negative potentials by the addition of ammonia or alaninate. This was ascribed to the formation of a mixed ligand chelate involving ammonia or the alaninate ion. From the relation between the shift of the half-wave potential and the concentration of ammonia or alaninate, the composition and the stability constant of the mixed ligand chelate were determined and the electrode reaction was established as:

$$\begin{array}{l} \mathrm{Cd(A)Z^{2-\mathit{m}}} \rightleftharpoons \mathrm{CdZ^{2-}} + n\mathrm{H^+} + \mathrm{Hg} + 2\mathrm{e^-} \rightleftharpoons \mathrm{Cd(Hg)} + \mathrm{H}_n\mathrm{Z}^{n-4} \\ \qquad\qquad\qquad\upharpoonleft\downharpoonright \\ \qquad\qquad\qquad\mathrm{CdZ_2{}^{6-}} \end{array}$$

where A means the ammonia or the alaninate ion. The K_2, $K^{\mathrm{NH_3}}$, and K^{ala} values determined were 5.5×10^2, 1.38×10^2, and 2.61×10^4 respectively.

The cadmium(II) chelates of ethylenediaminetetraacetic acid (EDTA) and its related compounds have been studied by numerous investigators.[1–4] The cadmium(II) chelates of several aminopolycarboxylic acids have been found to give two waves frequently. The reversible first wave is kinetic in

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1) N. Tanaka, R. Tamamushi and M. Kodama, *Z. Phys. Chem., N. F.*, **14**, 141 (1958).

2) J. Koryta, *Collection Czech. Chem. Commun.*, **24**, 3057 (1959).

3) N. Tanaka, K. Ebata, T. Takahari and T. Kumagai, This Bulletin, **35**, 1836 (1962).

4) Y. Koike and H. Hamaguchi, *J. Inorg. Nucl. Chem.*, **29**, 437 (1967).

nature and may be attributed to the reduction of the cadmium(II) ion dissociated from the cadmium(II)-aminopolycarboxylate chelate. The second wave, which corresponds to the direct reduction of the cadmium(II)-aminopolycarboxylate chelate is, however, irreversible. Generally, the direct reduction of the cadmium(II)-aminopolycarboxylate chelate is irreversible. Therefore, the polarographic wave due to the direct reduction of the cadmium(II)-aminopolycarboxylate chelate can hardly be used for the establishment of the electrode reaction mechanism or for the determination of an equilibrium between the cadmium(II) ion and aminopolycarboxylate. Exceptionally, the cadmium(II) chelate of ethylenediaminetetrapropionic acid (EDTP) was found to behave reversibly in a polarographic electrolysis. In this paper, the polarographic behavior of the cadmium(II) ion in the EDTP solution will be investigated systematically and the solution equilibria between the cadmium(II) ion and EDTP will be determined.

The effects of ammonia and the alaninate ion on the polarographic behavior of the cadmium(II)-EDTP chelate were also studied. The half-wave potential of the cadmium(II)-EDTP chelate shifted to more negative potentials with an increase in the concentration of ammonia or the alaninate ion. This was ascribed to the formation of a mixed ligand chelate involving ammonia or the alaninate ion.

Experimental

Reagents. The purification of EDTP and the preparation of its solution have been described previously.[5] The methods of preparing and standardizing a cadmium(II) perchlorate solution were also given in a previous paper.[6] All the other chemicals were of an analytical reagent grade and were used without further purification. The ionic strength of the sample solution was adjusted to 0.30 by adding an appropriate volume of a 1.0 M sodium perchlorate solution. The alanine used in this study was a racemic mixture.

Apparatus and Experimental Procedure. All the apparatus (mannual and pen-recording polarographs and the dropping mercury electrode (DME)) and the experimental procedures were the same as those employed previously.[5] All the polarographic measurements were conducted at 25°C.

Results and Discussion

Polarographic Behavior of the Cadmium(II) Ion in an Ethylenediaminetetrapropionate Solution in the Absence of Ammonia or Alaninate. The d. c. polarographic behavior of the cadmium(II) ion in an EDTP solution not containing ammonia or alaninate was studied in the pH range from 8.30 to 10.30. In the present study, no buffer reagent was used, because the present system always contains a large excess of un-complexed EDTP over cadmium(II) ions and, hence, is considered to have enough of a buffer capacity to maintain the pH value of the solution constant in this pH range. Over the entire pH range employed, the cadmium(II) ion invariably gave a well-defined single wave. A typical polarogram is reproduced in Fig. 1. As is shown in Fig. 2, a conventional plot of $\log(i/(i_l-i))$ against the applied d.c.

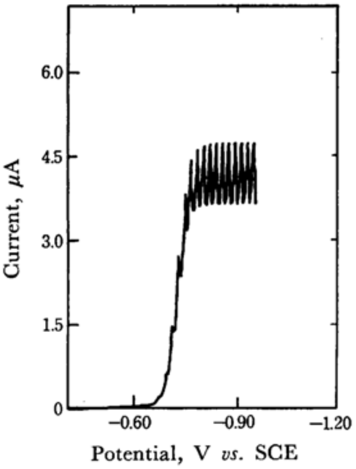

Fig. 1. D. c. polarogram of cadmium(II) ion in EDTP solution.
$\mu=0.30$, pH$=9.31$
Concentration of cadmium(II)$=0.920$ mM
Concentration of EDTP$=20.0$ mM

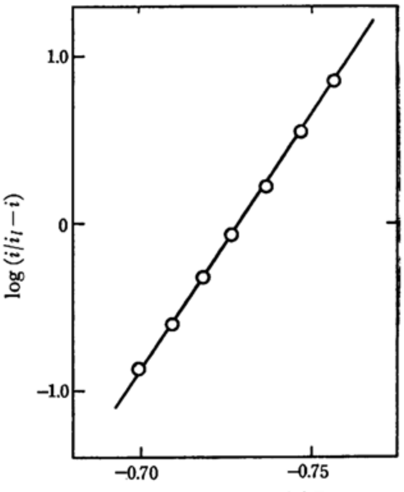

Fig. 2. A conventional plot of $\log(i/(i_l-i))$ against the applied d. c. potential.
$\mu=0.30$, pH$=9.31$
Concentration of cadmium(II)$=0.920$ mM
Concentration of EDTP$=20.0$ mM

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[5] M. Kodama and A. Kimura, This Bulletin, **40**, 1639 (1967).

[6] M. Kodama and C. Sasaki, This Bulletin, **41**, 127 (1968).

potential, E, gave straight lines with reciprocal slopes falling in the range from 32 to 35 mV. This clearly indicates that the electrode reaction is a reversible two-electron reduction process.

The wave-height was found to be exactly proportional to the bulk concentration of the cadmium(II) ion and the square-root of the effective pressure on the DME (The results are not shown here). These facts also support the above conclusion that the electrode reaction of the cadmium(II) ion in EDTP solution proceeds reversibly.

In the present pH range, the wave-height was almost independent of the pH value of the sample solution and the concentration of un-complexed EDTP, but slightly lower than that observed in an acid medium. The decrease in the wave-height may correspond to the chelate formation of the cadmium(II) ion with EDTP, because the diffusion-current constant of a complexed metal ion is usually smaller than that of un-complexed metal ion.

An EDTP is a weak acid with $pK_1=2.96$, $pK_2=3.32$, $pK_3=6.58$, and $pK_4=9.33$,[7,8] where the pK's are the acid dissociation constants of EDTP. Therefore, the conditional formation constant of the cadmium(II)-EDTP chelate must be a function of the hydrogen ion concentration; hence, the half-wave potential of the cadmium(II) ion in an EDTP solution would greatly depend on the pH value of the solution. This prediction was examined experimentally. Some typical results are shown in Table 1. The half-wave potential shifted to more negative potentials with an increase in the pH value of the solution. As was discussed in connection with the polarography of the copper(II)-*N*-(2-hydroxyethyl)-ethylenediamine-*N,N′,N′*-triacetate chelate,[9] when only a normal chelate with a 1-to-1 composition is formed, the half-wave potential, $(E_{1/2})_{\mathrm{CdZ}}$ may be expected to shift to negative potentials with a decrease in the log (α_{H}) value of EDTP, log $(\alpha_{\mathrm{H}})_Z$, corresponding to the following relation:

$$\frac{\Delta(E_{1/2})_{\mathrm{CdZ}}}{\Delta \log(\alpha_{\mathrm{H}})_Z} = 29.6\,\mathrm{mV} \qquad (1)$$

Here, $(\alpha_{\mathrm{H}})_Z$ is given by $1+[\mathrm{H}^+]/k_4+[\mathrm{H}^+]^2/k_4\cdot k_3+\cdots+[\mathrm{H}^+]^4/k_4k_3k_2k_1$ and k's are the dissociation constants of EDTP. As is shown by the data in Table 1, however, the negative shift of the half-wave potential with a decrease in the log $(\alpha_{\mathrm{H}})_Z$ value was much greater than that expected from the (1) relation.

The dependence of $(E_{1/2})_{\mathrm{CdZ}}$ on the concentration of EDTP was also investigated. The results are given in Table 2. $(E_{1/2})_{\mathrm{CdZ}}$ shifted to more negative potentials with an increase in the concentration of un-complexed EDTP, $[\mathrm{Z}]_f$. The shift of the half-wave potential, however, was much greater than that to be expected for the reversible two-electron reduction of the normal

TABLE 1. $(E_{1/2})_{\mathrm{CdZ}}$ AND pH

$\mu=0.30$, Concentration of EDTP=20.0 mM
Concentration of cadmium(II)=0.920 mM

pH	log $(\alpha_{\mathrm{H}})_Z$	$(E_{1/2})_{\mathrm{CdZ}}$ V *vs.* SCZ	$\Delta(E_{1/2})_{\mathrm{CdZ}}$, mV Calcd (29.6 Δ log$(\alpha_{\mathrm{H}})_Z$)	Obsd
8.33	1.024	−0.695	0	0
8.84	0.612	−0.714	12.2	19
9.31	0.311	−0.729	21.1	34
9.69	0.158	−0.738	25.6	43
10.01	0.082	−0.743	27.9	48

TABLE 2. $(E_{1/2})_{\mathrm{CdZ}}$ AND $[\mathrm{Z}]_f$

$\mu=0.30$, pH=9.33
Concentration of cadmium(II)=0.920 mM

$[\mathrm{Z}]_f$	$(E_{1/2})_{\mathrm{CdZ}}$ V *vs.* SCE	$\Delta(E_{1/2})_{\mathrm{CdZ}}$, mV Calcd (29.6 Δ log$[\mathrm{Z}]_f$)	Calcd (with the aid of Eq. (3″))	Obsd
10.0	−0.710	0	0	0
20.0	−0.729	−8.9	−16.0	−19
30.0	−0.741	−14.1	−29.0	−31

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[7] R. C. Courtney, S. Chaberek, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, **75**, 4814 (1953).

[8] M. Kodama and Y. Tominaga, This Bulletin, **42**, 721, 724 (1969).

[9] M. Kodama and Y. Tominaga, *ibid.* **42**, 394 (1969).

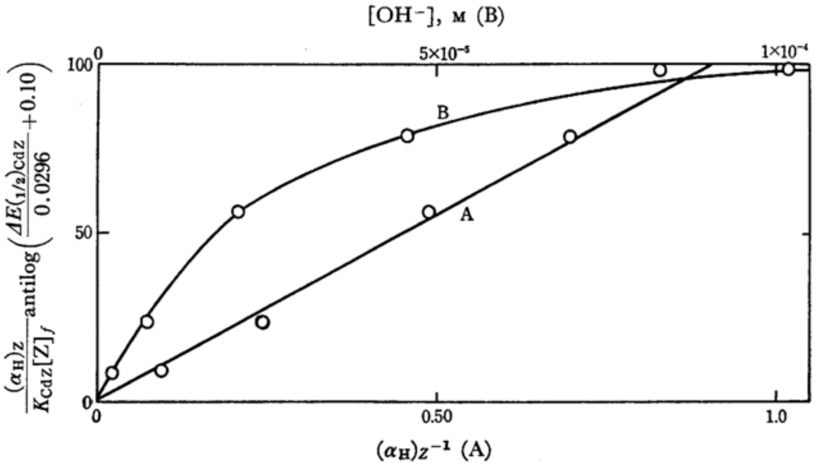

Fig. 3. The plot of $\frac{(\alpha_H)_Z}{K_{CdZ}[Z]_f}$ antilog$\left[\log\frac{k_{Cd^{2+}}}{k_{CdZ}}+\frac{\Delta(E_{1/2})_{CdZ}}{0.0296}\right]$ against $[Z]_f/(\alpha_H)_Z$ or $[OH^-]$.

chelate with a composition of 1-to-1, $\Delta(E_{1/2})/\Delta\log[Z]_f=-29.6$ mV.

Since the present study was conducted at higher pH's, the above two facts clearly indicate that, under the present experimental conditions, the cadmium(II) ion forms normal chelate with a 1-to-2 composition as well as that with a 1-to-1 composition with EDTP. Therefore, the electrode reaction can be assumed to be:

$$\begin{array}{l} CdZ^{2-} + nH^+ + Hg + 2e^- = Cd(Hg) + H_nZ^{n-4} \\ \quad\rightleftharpoons \\ CdZ_2^{6-} \end{array} \qquad (2)$$

with the half-wave potential corresponding to:

$$(E_{1/2})_{CdZ} = E^\circ_{Cd} + 0.0296\left[\log f_{Cd^{2+}} + \log\frac{k_{Cd(Hg)}}{k_{CdZ}} - \log\frac{K_{CdZ}}{(\alpha_H)_Z}\left(1+\frac{K_2}{(\alpha_H)_Z}[Z]_f\right)[Z]_f\right] \qquad (3)$$

where E°_{Cd}, $f_{Cd^{2+}}$, $k_{Cd(Hg)}$, k_{CdZ}, and K_{CdZ} have their usual meanings and where $K_2=[CdZ_2^{6-}]/[CdZ^{2-}]\cdot[Z^{4-}]$.

From Eq. (3), the shift of the half-wave potential of the cadmium(II) ion due to the chelate formation with EDTP, $\Delta(E_{1/2})_{CdZ}$, can be derived as:

$$\Delta(E_{1/2})_{CdZ} = 0.0296\left[\log\frac{k_{CdZ}}{k_{Cd^{2+}}} + \log\frac{K_{CdZ}}{(\alpha_H)_Z}\left(1+\frac{K_2[Z]_f}{(\alpha_H)_Z}\right)\right] \qquad (3')$$

By rearranging Eq. (3′) and by casting the resulting relation into antilog form, (3″) can be easily derived:

$$1+\frac{K_2}{(\alpha_H)_Z}[Z]_f = \frac{(\alpha_H)_Z}{K_{CdZ}[Z]_f} \times \text{antilog}\left[\log\frac{k_{Cd^{2+}}}{k_{CdZ}}+\frac{\Delta(E_{1/2})_{CdZ}}{0.0296}\right] \qquad (3'')$$

On the other hand, if the fact that the shift of the half-wave potential is much greater than that to be expected for the reversible two-electron reduction of the chelate with a 1-to-1 composition can be ascribed to the formation of a mixed ligand chelate involving the hydroxyl ion, OH^-, the left-hand side of Eq. (3″) should be replaced by $1+K^{OH}\cdot[OH^-]$, where K^{OH} is $[CdZ(OH)^{3-}]/[CdZ^{2-}]\cdot[OH^-]$. Using some typical data, the right-hand side of Eq. (3″) was plotted against $[Z]_f/[\alpha_H]_Z$ or $[OH]^-$. As is shown in Fig. 3, only the plot of the right-hand side of Eq. (3″) against $[Z]_f/(\alpha_H)_Z$ gave a linear relation with an intercept of 1. Furthermore, as is shown by the data in Table 2, with the increase in the concentration of un-complexed EDTP, the half-wave potential was found to shift to more negative potentials corresponding exactly to Eq. (3″). These facts strongly confirm the formation of a normal chelate with a composition of 1-to-2 and, hence, the electrode reaction (2). In the calculation of the right-hand side of Eq. (3″) the K_{CdZ} value of 2.51×10^5 ($\mu=0.30$) estimated from the K_{CdZ} value obtained in a solution with an ionic strength of 0.10 by Courtney *et al.*[7] and the activity coefficients of the ion calculated by means of the Davies equation[10] were used. From the slope of the linear relation in Fig. 3, K_2 was estimated to be 5.5×10^2.

D.C. Polarographic Behavior of the Cadmium(II) Ion in EDTA Solutions Containing Ammonia or Alanine. The d.c. polarographic behavior of the cadmium(II) ion in EDTP solutions containing ammonia or the alaninate ion was also investigated systematically. The limiting current of the cadmium (II)-EDTP chelate was little affected by the presence of ammonia or the alaninate ion, but the half-wave potential was found to shift to more negative potentials with an

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[10] J. N. Butler, "Ionic Equilibrium," Addison-Wesley Publishing Co., Reading, Massachusetts (1964), p. 437.

increase in the concentration of ammonia or alaninate. Considering the magnitude of formation constants of cadmium(II)-ammine, -alaninate, and -EDTP complexes,[11] it may safely be concluded that even 0.1 M ammonia or alaninate ions can not displace the EDTP anion from the cadmium(II)-EDTP chelate under the present experimental conditions. The conditional formation constant of the mixed ligand chelate involving both EDTP and ammonia or the alaninate ion is larger than that of the normal EDTP chelate, and in the polarography of the metal complexes, the increase in the value of the conditional formation constant always results in a negative shift of the half-wave potential. Therefore, the above negative shift caused by the addition of ammonia or the alaninate ion can be attributed to the formation of a mixed ligand chelate involving ammonia or the alaninate ion.

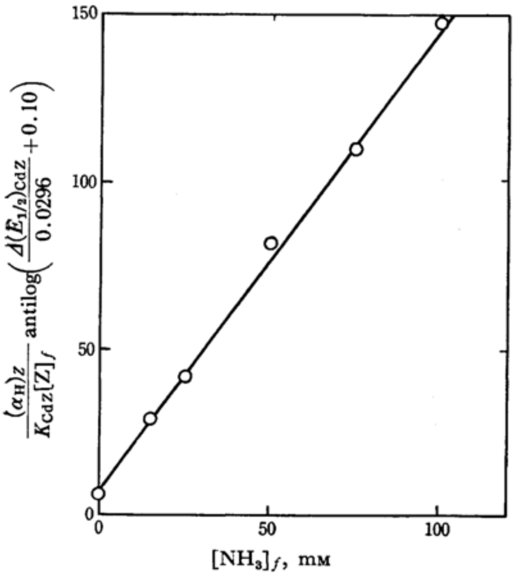

Fig. 4. The plot of $\frac{(\alpha_H)_Z}{K_{CdZ}[Z]_f}$ antilog$\left[\log\frac{k_{Cd^{2+}}}{k_{CdZ}}+\frac{\Delta(E_{1/2})_{CdZ}}{0.0296}\right]$ against $[NH_3]_f$.
pH=9.33, Concentration of EDTP=20.0 mM

If a mixed ligand chelate with the composition of $Cd(A)Z^{2-m}$ is also formed (where A indicates ammonia or the alaninate ion), the left-hand side of Eq. (3'') should be replaced by $1+K_2[Z]_f/(\alpha_H)_Z+K^A[A]_f$. Here, K^A denotes $K^{NH_3}=[Cd(NH_3)Z^{2-}]/[CdZ^{2-}][NH_3]_f$ of $K^{ala}=[CdZ(ala)^{3-}]/[CdZ^{2-}][ala]_f$, and $(A)_f$ denotes the concentration of un-complexed ammonia, $[NH_3]_f$ or that of the un-complexed alaninate ion, $[ala]_f$. Therefore, provided that the concentration of un-complexed EDTP and the solution pH are kept constant, the plot of the right-hand side of Eq. (3'') against $[A]_f$ will give a linear relation with a intercept of $1+K_2[Z]_f/(\alpha_H)_Z$. This relation was examined successfully by means of the experimental data. The results are shown in Figs. 4 and 5. From the slopes of the linear relations in Figs. 4 and 5, K^{NH_3} and K^{ala} were estimated to be 1.38×10^2 and 2.61×10^4 respectively. On the basis of the above results and discussion, the electrode reaction of the cadmium(II)-EDTP chelate at the mercury electrode in the presence of ammonia

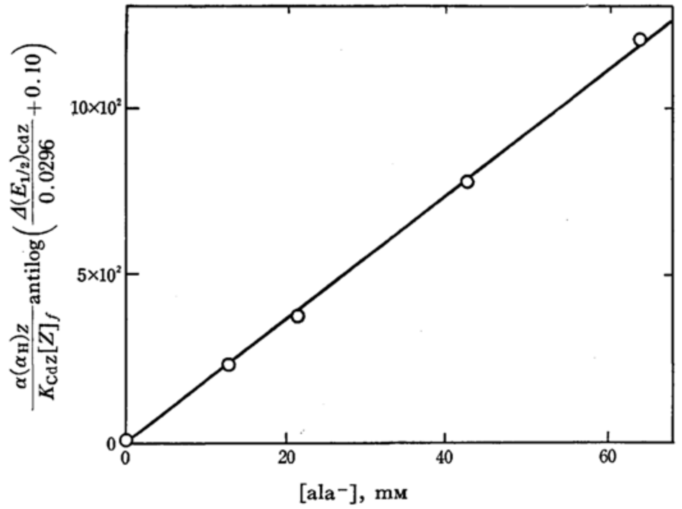

Fig. 5. The plot of $\frac{(\alpha_H)_Z}{K_{CdZ}[Z]_f}$ antilog$\left[\log\frac{k_{Cd^{2+}}}{k_{CdZ}}+\frac{\Delta(E_{1/2})_{CdZ}}{0.0296}\right]$ against $[ala]_f$.
pH=9.45, Concentration of EDTP=10.0 mM

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[11] L. G. Sillen and A. E. Martell, "Stability Constants of Metal Ion Complexes," The Chemical Society, London (1964).

or the alaninate ion can be established to proceed thus:

$$\begin{array}{lll} \mathrm{Cd(A)Z}^{2-m} & \rightleftharpoons \mathrm{CdZ}^{2-} + n\mathrm{H}^{+} + \mathrm{Hg} + 2e^{-} & \\ & \quad \upharpoonleft\downharpoonright & \\ & \quad \mathrm{CdZ_2}^{6-} & \\ & \rightleftharpoons \mathrm{Cd(Hg)} + \mathrm{H}n\mathrm{Z}^{n-4} & (4) \end{array}$$

where $\mathrm{Cd(A)Z}^{2-m}$ means $\mathrm{Cd(NH_3)Z}^{2-}$ or $\mathrm{CdZ(ala)}^{3-}$.

Here, it can be mentioned that the K^{ala} value found was almost identical with the K_1 value of the cadmium(II) - alaninate chelate.[12] If an alaninate anion functions as a monodentate ligand in the present mixed ligand-chelate formation, the equilibrium constant, K^{ala}, can be expected to be considerably smaller than the K_1 value of cadmium(II)-alaninate chelate. As has been reported by several authors,[11] K_1 values of cadmium(II) complexes of monodentate ammonia and the acetate ion can be expected to be thermodynamically considerably smaller than that of the cadmium(II) chelate of the bidentate alaninate anion. The steric and other effects may also reduce the stability of the mixed ligand chelate appreciably. Therefore, the above fact may indicate that an alaninate anion acts as a bidentate ligand in the present mixed-ligand-chelate formation.

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[12] D. J. Perkins, *Biochem. J.*, **57**, 702 (1954).