2 orders of magnitude smaller than for perylene, for example? Work and double-layer corrections are unlikely to significantly alter these findings, and solvent reorganization energies should be similar. This suggests inner-sphere reorganizational energies for **1** and DBCOD are larger than for aromatic compounds. Calculations indicate that changes in geometry in going from benzene (a simple aromatic model system) to its anion radical are small,[18] while Dewar and co-workers[19] predict that bond alteration decreases in the anion radical of COT compared with the neutral molecule. Formation of such a symmetric anion radical would require considerable changes in bond lengths affording larger activation energies. This rationale is also consistent with our qualitative findings[20] that the second electron transfer to **1** is faster than the first. Since major structural changes occur at the first wave, little additional distortion is required to form the expected symmetric dianion.

A final comment regarding the origin of the oxidizing power of **1** is in order. Its reduction potential is almost the same as the reduction of the *cation radical* of tri-*tert*-butylpentalene, **2** (0.75 V), also a planar 8 π electron molecule.[21] Comparison of the reduction potential of **1** with **2** (−1.4 V) and DBCOD (−1.61 V) eliminates strain or antiaromaticity as major factors. Obviously the 16 fluorine atoms must play an important role here. While we are unaware of an appropriate model system that would allow evaluation of the substituent effect, it is worth noting that both decafluorobiphenyl[22] and tetrafluorotetracyanoquinodimethane[12] reduce more positive than the parent molecules by ca. 0.1 V per fluorine atom.

We are currently examining a series of fluorinated model compounds to gain better insight into the energetics for reduction of **1**.

Acknowledgment. We thank EG and G for the loan of a PAR 174/50 ac interface and Dr. Bob Glosser for use of his PAR 128A lock-in amplifier. This work was aided by Grants AT-748, AT-646, and AF-585 from the Robert A. Welch Foundation. Helpful discussions with Albert J. Fry, Donald E. Smith, and Ronald, H. Fleming are gratefully acknowledged.

Registry No. 1, 42858-85-5; ferrocene, 102-54-5.

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Dynamic Features of the Ethylenediaminetetraacetate Complexes in Aqueous Solutions Studied by the Ultrasonic Absorption Method. 2. Zn and Cd Complexes

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Abstract: Ultrasonic relaxation absorption was observed in aqueous solutions of zinc and cadmium ethylenediaminetetraacetate (EDTA) complexes. The absorption was ascribed to the rapid structural change of the EDTA complex, i.e., pentacoordinate structure $\rightleftharpoons$ hexacoordinate structure (k_f, k_b). The proportions of the two structures were evaluated from the absorption amplitude. In the case of the Cd complex, the stability of the hexacoordinate structure is much larger than those of the Zn and alkaline-earth complexes. The rate constant k_f was found to be closely related to the water-substitution rate constant of the metal ion. A reaction mechanism with a steady-state intermediate is proposed.

Metal chelates of EDTA have received much attention and have been studied by a variety of techniques. However, their structures and kinetic properties in solution are still ambiguous. Concerning them, one of the most fundamental and important problems might be that of how many coordinating groups of EDTA bind to the metal ion. To date, many conflicting results have been proposed for the problem.[1-12]

For the study of the dynamic features of the complex in solution, the ultrasonic absorption measurement is one of the most valuable techniques. As far as we are aware, few ultrasonic absorption studies have been made on either EDTA[13] or its metal complexes.[14,15] In a previous paper,[15] we have applied the ultrasonic absorption method to the Co(II)– and alkaline-earth–EDTA complex solutions, proposed a mechanism for the reaction of the pentacoordinate structure $\rightleftharpoons$ hexacoordinate structure, and given the kinetic parameters. An accumulation of much more information is required in order to establish the clear structure of the complex in solution. Along this line, the present work was undertaken to obtain the static and kinetic information for the Zn– and Cd–EDTA complexes on the basis of the results obtained in the previous work.

Experimental Section

Materials. Reagent Grade zinc and cadmium nitrates and K_2EDTA were used without further purification. Solutions were prepared by mixing the desired amounts of metal nitrates, K_2EDTA, and KOH in a mole ratio of 1:1:2, and the final pH was adjusted to 6.5 by dropwise addition of KOH or HNO_3 solution. The ionic strength was adjusted to

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Table I. Ultrasonic Absorption Parameters of the Zn– and Cd–EDTA Systems at pH 6.5, 25.0 °C, and Ionic Strength of 3.0

	ΣC_{MY}, M	$A \times 10^{17}$, cm^{-1} s^2	$B \times 10^{17}$, cm^{-1} s^2	f_r,[a] MHz	$v \times 10^{-5}$, cm s^{-1}	ρ, g cm^{-3}	$(\alpha'\lambda)_{max}$[b] 10^3
Zn	0.10	837	27	1.5	1.593	1.180	1.0
	0.20	1580	30	1.6	1.597	1.187	2.0
	0.30	2370	32	1.7	1.605	1.193	3.2
	0.40	3570	35	1.5	1.609	1.198	4.4
	0.50	4750	39	1.5	1.615	1.204	5.7
	0.60	6060	43	1.5	1.625	1.212	7.2
Cd	0.30	134	30	4.6	1.598	1.206	0.5
	0.40	201	33	5.3	1.602	1.216	0.9
	0.50	325	38	4.9	1.606	1.226	1.3
	0.60	450	49	4.8	1.621	1.240	1.8

[a] Relative errors: Zn (0.10 M) ±30%, Zn (0.20~0.60 M) ±8%, Cd(0.30~0.60 M) ±6%. [b] Relative errors: Zn (0.10 M) ±36%, Zn (0.20~0.60 M) ±7%, Cd (0.30~0.60 M) ±4%.

3.0 by the addition of KNO_3. Deionized and distilled water was used for all solutions.

Measurements. Ultrasonic absorption was measured by the pulse method in the frequency range 1.5–95 MHz. Details of the apparatus have been described elsewhere.[16] The velocity of sound was measured by a "sing-around" method at 1.92 MHz. The temperature was controlled at 25.0 °C.

Results and Discussion

In all solutions of Zn– and Cd–EDTA systems, ultrasonic relaxation absorptions were observed and were characterized by a single-relaxation equation,

$$\alpha/f^2 = \frac{A}{1 + (f/f_r)^2} + B \qquad (1)$$

where α is the absorption coefficient, f is the frequency, f_r is the relaxation frequency, and A and B are the relaxation and nonrelaxation absorptions, respectively. The absorption parameters f_r, A, and B were determined by fitting the experimental data to eq 1 by means of a nonlinear root-mean-square method. Parameter A is related to the maximum excess absorption per wavelength by eq 2, where α' is the excess absorption coefficient,

$$(\alpha'\lambda)_{max} = (A/2)f_r v \qquad (2)$$

λ is the wavelength, and v is the velocity of sound.

Representative absorption spectra of Zn– and Cd–EDTA complexes are shown in Figure 1. The measurements were carried out in each system with changes in the pH and the complex concentration. No effect of pH on the absorption was observed in the range of pH 4–8. The absorption parameters obtained are summarized in Table I together with the experimental conditions. The results in the table show at least two features. One is the independence of the f_r values on the complex concentration, and the other is the monotonic increase of $(\alpha'\lambda)_{max}$ with the complex concentration. These results lead to the prediction that the present relaxation absorption is due to the intramolecular reaction of the metal–EDTA complex.

For the intramolecular reaction 3, f_r and $(\alpha'\lambda)_{max}$ are given by eq 4 and 5, respectively, where K is the equilibrium constant, k_f and k_b are the rate constants of the forward and backward reactions, respectively, β_0 is the adiabatic compressibility, ΔV is the volume change of the reaction, $\sum C_{MY}$ is the total concentration of the complex, and the subscripts * and ** mean two different forms of the complex. The experimental result that f_r is independent of the complex concentration can be satisfactorily interpreted by eq 4 since this equation has no concentration term.

$$MY_{*} \underset{k_b}{\overset{\overset{(K)}{k_f}}{\rightleftharpoons}} MY_{**} \qquad K = k_f/k_b \qquad (3)$$

$$2\pi f_r = k_f + k_b \qquad (4)$$

$$(\alpha'\lambda)_{max} = \frac{\pi \Delta V^2}{2\beta_0 RT} \frac{K}{(1 + K)^2} \sum C_{MY} \qquad (5)$$

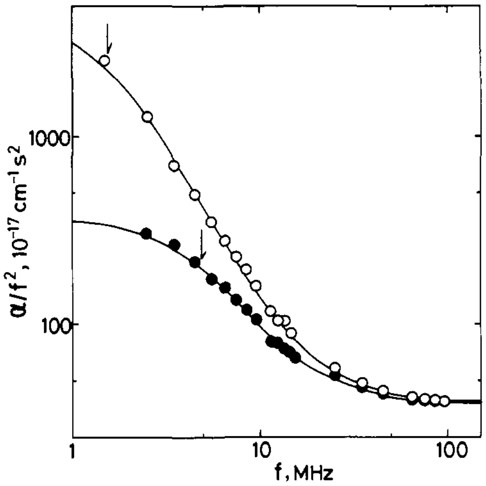

Figure 1. Ultrasonic absorption spectra of the Zn– and Cd–EDTA solutions at 0.5 M, pH 6.5, 25.0 °C, and ionic strength 3.0: (○) Zn–EDTA, (●) Cd–EDTA. The arrows indicate the relaxation frequency.

Equation 5 suggests the experimental result that the plots of $\beta_0(\alpha'\lambda)_{max}$ vs. $\sum C_{MY}$ give a straight line that goes through the origin of the coordinates as shown in Figure 2. The above results are in complete agreement with those of the previous work in which the absorption has been successfully ascribed to the rapid equilibration of the penta- and hexacoordinate structures of the EDTA complex. Supplementally, the following reactions have been examined as the origin of the present relaxation absorption; (1) rotational isomerization of $EDTA^{4-}$ anion,[13] (2) complex formation of metal cation and $EDTA^{4-}$ anion, (3) protonation or hydrolysis of the metal–EDTA complex anion (MY^-), and (4) ionpair formation of K^+ and MY^-. All of these possible reactions, however, are discarded due to the fact that either some of the reactant concentrations are too low to expect a detectable absorption or the concentration dependences of the relaxation parameters predicted for the reactions are inconsistent with the observed results. Consequently, it may be concluded that the present relaxation absorption is based on the intramolecular reaction of the metal–EDTA complex.

When we survey the detailed mechanism of reaction 3, it is very interesting to note that the sequence of the f_r values of Zn– and Cd–EDTA systems, including those of Co(II)– and alkaline-earth–EDTA systems, (f_r(MHz); Mg ($\ll$1) $\ll$ Zn (1.5) < Co (1.9) < Cd (5.0) < Ca (8.0) < Sr (21) < Ba (33)) is just the same as that of the water-substitution rate constants (k_{H_2O}) of the corresponding metal ions[17-21] (k_{H_2O} (10^8 s^{-1}); Mg (10^{-3}) $\ll$ Zn

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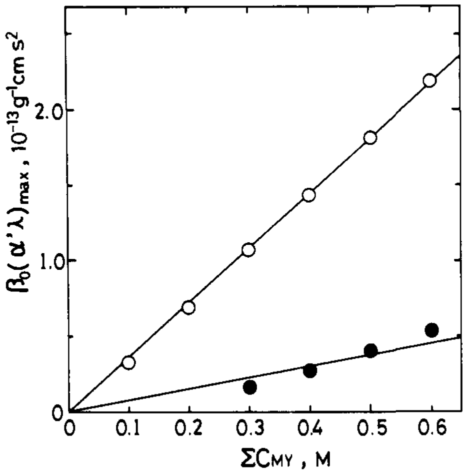
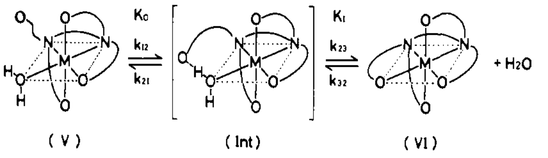


Figure 2. Plots of $\beta_0(\alpha'\lambda)_{max}$ vs. $\sum C_{MY}$ for the Zn– and Cd–EDTA solutions at pH 6.5, 25.0 °C, and ionic strength 3.0: (○) Zn–EDTA, (●) Cd–EDTA.

(0.32) < Co (0.65) < Cd (2.5) < Ca (3.0) < Sr (3.5) < Ba (7.2)). This fact strongly suggests that the substitution of the coordinated water is rate determining in reaction 3. Summarizing the above facts, we ascribed the present absorption to the reaction



(6)

$$K_{V-VI} = K_0K_1 \tag{7}$$

where V is the pentacoordinate complex, Int is the intermediate with an intramolecular hydrogen bond between the carboxylate group and the coordinated water, and VI is the hexacoordinate complex. V, VI, and K_{V-VI} correspond to MY•, MY••, and K in reaction 3, respectively.[22] If we assume the species Int is in a steady state, the relaxation equation for reaction 6 is given by

$$2\pi f_r = \frac{k_{12}k_{23}}{k_{21} + k_{23}} + \frac{k_{21}k_{32}}{k_{21} + k_{23}} \tag{8}$$

In the case of $k_{21} \gg k_{23}$,[22] the above equation leads to

$$2\pi f_r = \frac{k_{12}}{k_{21}}k_{23} + k_{32} = K_0k_{23} + k_{32} \tag{9}$$

Since the equilibrium constant K_0 is not related to the inner coordination sphere directly, it was assumed to be constant as long as the charge of the central metal was the same. So $K_0 = 0.14$, which was evaluated in the previous work,[15] was used in the calculation of the rate constants. In order to calculate the rate constants of reaction 6, we must estimate the value of K_{V-VI}. For some of the metal–EDTA systems, K_{V-VI} have been reported.[9] Unfortunately, however, it is still not known for the Zn– and Cd–EDTA systems.

If the value of ΔV were given, K_{V-VI} could be calculated from the slope of the plot of $\beta_0(\alpha'\lambda)_{max}$ vs. $\sum C_{MY}$ as seen in eq 5. In the previous work,[15] the values of ΔV were obtained to be Co (4.9 cm^3 mol^{-1}), Ca (5.3 cm^3 mol^{-1}), Sr (3.6 cm^3 mol^{-1}), and Ba (5.4 cm^3 mol^{-1}). For both Zn– and Cd–EDTA systems, we assumed $\Delta V = 5$ cm^3 mol^{-1} from an average of the above values with the assumption that ΔV is independent of the central metal ions. With the use of this value and the slopes in Figure 2, the values of K_{V-VI} for the Zn– and Cd–EDTA systems were determined to be 2.0 and 21, respectively. In other words, in the case of the Zn complex, pentacoordinate structure and hexacoordinate structure exist in proportions of about 30% and 70%, respectively, and these values are close to those of the Co(II) and alkaline-earth complexes. On the other hand, the Cd complex exists predominantly in the form of the hexacoordinate structure at about 95%. It is interesting that, though Zn and Cd ions have similar electron configuration, the stability of the hexacoordinate structure is an order of magnitude greater in Cd–EDTA complex than that in Zn–EDTA complex.

In order to see the contribution of the sixth coordination group of EDTA to the stability of the hexacoordinate complex, we compared the overall stability constants of the complexes of EDTA with those of the homologous pentadentate ligand, *N*-hydroxyethylethylenediamine-*N,N′,N′*-triacetate (HEDTA). This comparison was performed not only for the Zn and Cd complexes but also for the complexes of Co(II) and alkaline earths, and the values of K_{EDTA}/K_{HEDTA} are listed in Table II. In this table we can see that for almost all metals, including Zn, the EDTA complex is about 2 orders of magnitude more stable than the HEDTA complex. In the case of Cd, however, the EDTA complex is 3 orders of magnitude more stable. These facts are coincident with the large stability of the hexacoordinate structure of the Cd–EDTA complex.

More interesting information can be obtained by comparing the stability constants of Zn and Cd complexes of the homologous multidentate ligands. The values in Table III show that an increase of the stability constant is induced when the numbers of the coordinating groups of the ligand are increased by one. It is easy to see that the contributions of the *n*th coordination group are similar in the cases of Zn and Cd complexes when $n = 3$, 4, and 5. When $n = 6$, however, the Cd complex is 1.5 orders of magnitude more stable than the Zn complex. The above data further demonstrate that reaction 3 is the equilibrium: pentacoordinate structure $\rightleftharpoons$ hexacoordinate structure.

With the values of K_0, K_{V-VI}, and f_r, the rate constants k_{23} and k_{32} were calculated from eq 7 and 9 and are listed in Table IV together with the water-substitution rate constants k_{H_2O} of the corresponding metal ions. As shown in Table IV, the values of

Table II. Equilibrium Constants K_{V-VI} of the M(II)–EDTA Complexes and Ratio of the Stability Constants[a] of EDTA and HEDTA Complexes

	Co	Ni	Cu	Zn	Cd	Ca	Sr	Ba
K_{V-VI}	3.2[b]	3.0[b]	1.6[b]	2.0[c]	21[c]	2.3[d]	2.3[d]	2.3[d]
$(K_{EDTA}/K_{HEDTA}) \times 10^{-2}$	0.8	0.4	0.3	1.0	32	1.3	0.8	1.3

[a] Reference 23. [b] Reference 9. [c] This work. [d] Reference 15.

Table III. Ratio of the Stability Constants of the Zn and Cd Complexes of Multidentate Ligands

	$\log K_n/K_{n-1}$[a] for n[b] =			
	6	5	4	3
Zn	2.0	2.6	4.9	1.6
Cd	3.5	2.4	5.2	1.6

[a] K_n is the stability constant of the metal complex of the n-dentate ligand.[23] [b] The number of the coordinating groups of the ligand: $n = 6$, EDTA; $n = 5$, HEDTA; $n = 4$, ethylenediamine-*N,N′*-diacetate; $n = 3$, iminodiacetate; $n = 2$, glycine.

Table IV. Kinetic Parameters for Reaction 6 at 25.0 °C and Ionic Strength of 3.0

	$k_{23} \times 10^{-7}$, s^{-1}	$k_{32} \times 10^{-7}$, s^{-1}	$k_{H_2O} \times 10^{-7}$, s^{-1}
Zn–EDTA	4.6	0.32	3.2[a]
Cd–EDTA	21.0	0.14	25.1[a]

[a] Reference 17.

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[22] Since the hydrogen-bond formation is very fast, the reaction V → Int will be rate determined by the rotation about the N–CH$_2$COO$^-$ bond. The rate constant of this rotation (k_{12}) is in the order of 10^8 s^{-1}.[13] With the relationship $k_{21} = k_{12}/0.14$, k_{21} is supposed to be in the order of 10^9 s^{-1}. Consequently, we can deduce the condition of $k_{21} \gg k_{23}$ $(= k_{H_2O})$.

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k_{23} are in good agreement with k_{H_2O} of the corresponding metal ions. This fact suggests that in the present systems, like the Co(II)- and alkaline-earth–EDTA systems, the complex exists in two forms, pentacoordinate and hexacoordinate structures, and that the water-substitution process is the rate-determining process of the hexacoordinate complex formation. Furthermore, the consistent results obtained by use of the estimated values of K_0 and ΔV suggest the correctness of the estimation of these values.

Registry No. Cd-EDTA, 36077-58-4; Zn-EDTA, 12519-36-7.

On the Stability and Properties of Organic Metals and Their Isomeric Charge-Transfer Complexes

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Abstract: A methodology for conceptualizing the aggregation isomers of D–A adducts is presented. It is concluded that the mixed-stacks isomer . . .D–A–D–A. . . leads to *stabilization* of the *ground no-bond configuration.* On the other hand, the segregated-stacks isomer . . .DD||AA. . . leads to *stabilization of excited charge-transfer configurations* which form the delocalized state . . .$D^{+\rho}D^{+\rho}||A^{-\rho}A^{-\rho}$. . . with a partial degree of electron transfer (ρ). It is argued from first principles that this state is not always truly delocalized. In such cases, *there will be a barrier for electron hopping* (e.g., $A^-A \rightarrow AA^-$). A mechanism of curve-band crossing is responsible for stabilizing . . .$D^{+\rho}D^{+\rho}||A^{-\rho}A^{-\rho}$. . . below the no-bond state. The value of ρ in this isomer is determined by a combination of two factors: $I_D - A_A$ and the reorganization energy obtained by relaxing D^+ and A^- from the geometry of their neutrals. The recognition that the mixed-stacks isomer originates from a ground no-bond configuration, while the (often conducting) segregated-stacks isomer arises from crossing of the excited charge-transfer pack of configurations, indicates that the latter isomer could in principle be the less stable one. Experimental data are examined in light of the model.

Introduction

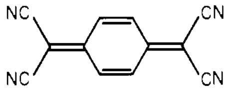
There are two classes of aggregation isomers within the ensemble of the D–A (donor–acceptor) adducts. The first type is the class of charge-transfer complexes,[1] in which the addends aggregate in mixed stacks of alternating donor (D) and acceptor (A) molecules:

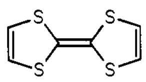
$$...D\text{–}A\text{–}D\text{–}A... \qquad (1)$$

The second class of D–A adducts involves complexes in which the donor and the acceptor molecules aggregate in segregated stacks as shown schematically in eq 2, where the double vertical line represents the segregation.

$$...D\text{–}D||A\text{–}A... \qquad (2)$$

The most attractive subset within the latter class is probably the group of organic metals,[2] among which the first and the best known member is the TTF·TCNQ (**1** and **2**) complex.[3] All the members of this subgroup aggregate in segregated stacks of donors and acceptors (eq 2), and many of them conduct electricity along the stacks in a metallic like fashion.[2] It is this feature which made them of special interest to chemists and physicists alike.


1 (TCNQ)


2 (TTF)

Our interest in this subgroup has been aroused since, from our experience in applying the charge-transfer model[1a] to organic reactions,[4] we reasoned that for D's and A's with moderate donor and acceptor abilities, the segregated stacks which characterize the organic metals should be a form which stabilizes an excited state of the D–A aggregate,[5] whereas the mixed stacks should be the form which stabilizes the ground state of the D–A aggregate. Therefore, we suspected that in principle organic metals may not necessarily be the most stable isomers, a point which has been raised before in one form or another by Perlstein,[2a] Torrance,[6a] and Sandman.[6b]

Further support of this point was provided by computational results[7] which show that the electrostatic energy for the TTF·TCNQ complex does not seem to be sufficient to stabilize any significant degree of electron transfer (ρ) from D to A. Since the experimentally determined ρ for TTF·TCNQ and other organic metals is ≥ 0.5,[8] then the mere existence of these stable organic metals is puzzling.

Thus we are facing here a complex problem. First of all, one would like to know what factors may influence the selection of the aggregation mode for a given D–A pair. An answer to this

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