breaking has also been reached by Dyke and Higginson[19] for the decomposition of the intermediate to products in the inner-sphere oxidation of $Co^{II}EDTA$ by $IrCl_6^{2-}$. That conclusion was reached on the basis of product distribution as a function of pH.

A similar effect as is observed here has been noted[20] for the rate of ring closure of Co^{III}(chelate)·Cl by elimination of chloride, as shown in Table VI. The CyDTA complex ring-closes very much faster than the EDTA complex.[21] By contrast, the rate of ring-closure[22] of $Co^{III}EDTA \cdot H_2O$ is slightly faster than for the analogous CyDTA complex.[20] This case, however, is complicated by the possibility of hydrogen bonding in the activated state and a strong acid-catalysis effect in the CyDTA complex.

Examination of Table VI reveals that the decomposition of I_1 to products for both chelates is more rapid than the rate of ring closure of corresponding chloro or aquo complexes and that this is due to a positive ΔS_2^* term, the ΔH_2^* terms being very similar. The increase in freedom in the activated state for our binuclear species may be partly due to the formation of a partial bond to the free acetate thereby neutralizing its charge and the resulting release of water of hydration, and partly to a significant lengthening of the Co-NCFe bond. The latter effect should increase ΔS_2^* because of separation of like charge and also as a result of a reduction in charge density which should release some of the oriented solvent.

Registry No. $[(EDTA)Co^{III}\text{-}NC\text{-}Fe^{II}(CN)_5]^{5-}$, 38531-79-2; $Fe(CN)_6^{3-}$, 13408-62-3; $Co^{II}EDTA^{2-}$, 14931-83-0; Co^{II}-$CyDTA^{2-}$, 28161-91-3; $[(CyDTA)Co^{III}\text{-}NC\text{-}Fe^{II}(CN)_6]^{5-}$, 38531-80-5.

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Interaction of Multidentate Cobalt(II)-Chelate Complexes with Ferricyanide Ion. II. Co^{II}DTPA (Diethylenetriaminepentaacetic Acid)

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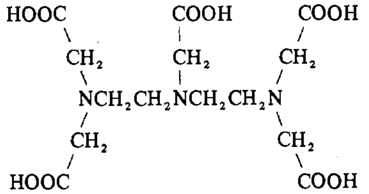
Diethylenetriaminepentaacetatocobaltate(II) [Co^{II}DTPA] is rapidly oxidized by ferricyanide ion to form a deep purple solution, and this color fades to a lighter solution. In this respect, the system is like the analogous Co^{II}EDTA- and Co^{II}-CyDTA-$Fe(CN)_6^{3-}$ systems. The rate of the slow reaction (decomposition of the cyano-bridged Co^{III}-Fe^{II} intermediate), however, is inversely dependent on $[H^+]$ in the pH range 5-7. The data are consistent with two structurally distinct forms of the complex. The experimental rate data adhere strictly to a derived rate law which takes into account these two forms of Co^{II}DTPA, one being hexadentate and the other pentadentate. The rate data follow both the concentration and acid dependence predicted by the rate law.

Introduction

The reaction scheme suggested by Adamson and Gonick[1] for the oxidation of ethylenediaminetetraacetatocobaltate(II) by ferricyanide ion has been substantiated by Huchital and Wilkins[2] and by work in this group.[3] The reaction involves an inner-sphere electron-transfer equilibrium step to a successor complex followed by the breakup of this complex to the final products. The driving force for the decomposition of this complex is the ring closure of the EDTA moiety.

It is now believed[4,5] that Co^{II}EDTA complexes are predominantly hexadentate in solution at pH 5. Therefore, the coordination between one of the acetate groups and the cobalt(II) must become broken as the cyano bridge forms. This same acetate group then slowly replaces the bridging ligand at the cobalt(III) center following electron transfer. Thus, any changes in the structure of the chelate group which affect the freedom of movement or the availability of the acetate groups should have a direct influence over the various steps in the reaction sequence. Such effects have been observed when *trans*-1,2-cyclohexanediaminetetraacetatocobaltate(II) [Co^{II}CyDTA] is the reductant.[3]

The multidentate ligand diethylenetriaminepentaacetic acid (DTPA)



$$(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)CH_2CH_2N(CH_2COOH)_2$$

contains eight possible coordination centers. The formation of a cyano-bridged intermediate by reaction of the cobalt(II) complex of this ligand with ferricyanide ion may result in a structure in which more than one unbound acetate group is available to replace the cyano bridge in the decomposition step. In addition this study may provide information about the structure of the cobalt complex of this ligand in solution, little of which is known at the present time.

In ligand substitution reactions between diethylenetriaminepentaacetic acid and nickel(II) complexes[6] and again in electron-transfer reactions between chromium(VI) and the

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[2] D. H. Huchital and R. G. Wilkins, *Inorg. Chem.*, 6, 1022 (1967).

[3] D. H. Huchital and R. J. Hodges, *Inorg. Chem.*, 12, 998 (1973).

[4] R. G. Wilkins and R. Yelin, *J. Amer. Chem. Soc.*, 89, 5496 (1967).

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cobalt(II) complex of diethylenetriaminepentaacetic acid,[7] the bulky nature of this ligand played an important part in the reactions. It is, therefore, likely that the cobalt(II) complex of this ligand can provide useful information in the present reaction.

Experimental Section

Materials. DTPA (Aldrich Chemical Co.) was purchased in the acid form and was found to be 99.45% pure by titration against a standard zinc solution at pH 5 using Xylenol Orange as indicator. Solutions were prepared as described previously.[3]

Kinetics Measurements. Formation and decomposition studies were performed under pseudo-first-order conditions as described previously.[3] $Co^{II}DTPA$ solutions were found to be air sensitive. Thus, solutions for spectral and kinetic analyses were purged for 1.5 hr prior to being used. Kinetic runs on the decomposition reaction were carried out in 5-cm quartz absorption cells with narrow openings which were fitted with serum caps. Deaerated cobalt(II) nitrate solution, DTPA, and sodium acetate–acetic acid were added (to bring the pH to the desired value and the ionic strength to 0.660). Ferricyanide ion was then injected into the system to initiate the reaction.

The rapid formation reactions were studied using stopped-flow techniques (Aminco-Morrow stopped-flow apparatus). The system was modified to allow the introduction of deaerated solutions.

The reactions were followed primarily at 420 nm. It was found that the slow decomposition of the intermediate was followed by a much slower secondary reaction and it was not possible to obtain a value for the final absorbance (A_∞) in the usual manner. Instead, the Manglesdorf method[8] was employed.

Results and Discussion

Qualitative tests show that $Co^{II}DTPA$ reacts rapidly with $Fe(CN)_6{}^{3-}$ to form a deep purple solution, and this color fades slowly to light purple. In this respect, the system is similar to that with $Co^{II}EDTA$ and $Co^{II}CyDTA$. The slow reaction, however, unlike the prior systems, is very pH dependent in the region pH 5–7. Initial rate measurements were carried out at three different acid concentrations and revealed that the observed first-order rate constant was inversely dependent on $[H^+]$ and that a change of *ca.* 0.8 pH unit produced *ca.* 300% change in k_{obsd}. It is clear that the correct rate law for this reaction must account for this strong dependence on acid concentration.

Potentiometric titrations have been carried out for DTPA complexes of a number of bivalent metal ions, including cobalt.[9-11] These results reveal that $Co^{II}DTPA^{3-}$ forms a dihydrogen species, $Co^{II}DTPA{\cdot}H_2{}^-$, with a pK_a of 3.51 at 20° (3.22 at 25°), and in addition, a monohydrogen species, $Co^{II}DTPA{\cdot}H^{2-}$, with a pK_a of 4.74 at 20° (4.94 at 25°). The pK_a for the dihydrogen complex agrees well with the pK_a of 3.0 for $Co^{II}EDTA{\cdot}H(H_2O)$[12] and the acid strength of these complexes is good evidence that the protonation occurs on a carboxylate group.[10] The pK_a for $Co^{II}CyDTA{\cdot}H(H_2O)$ is somewhat lower ($\sim$1.0)[13] due to the steric hindrance of the cyclohexyl ring. The pK_a of $\sim$5 for the $Co^{II}DTPA{\cdot}H^{2-}$ complex, however, has no counterpart in the EDTA or CyDTA systems. It is this difference, we believe, that is responsible for the strong pH dependence we observed in the present reaction.

No studies have yet been reported for the structure of $Co^{II}DTPA$ complexes in solution. Chabarek and coworkers,[10] however, have investigated the structure of the square-planar complex $Cu^{II}DTPA$. The relevance of their findings to the present system warrants a short discussion at this point, in order to lead the way to a derivation of a rate law for our reaction.

Chabarek believed that the difference between pK_a for the dihydrogen complex and that for the monohydrogen species for complexes such as $Cu^{II}DTPA$ ($\Delta pK_a = 1.77$) or $Co^{II}DTPA$ ($\Delta pK_a = 1.72$) is too great to consider that the less acidic proton could be attached to another carboxylate group. Instead, it is believed that this protonation occurs at the more basic amino nitrogen group. Evidence has been presented which supports this belief. Absorption spectra for $Cu^{II}DTPA{\cdot}H^{2-}$ and $Cu^{II}DTPA^{3-}$ compared with those of $Cu^{II}HEDTA^-$, $Cu^{II}dien^{2+}$, and $Cu^{II}trien^{2+}$ (the latter being representative of complexes in which two, three, and four nitrogen atoms, respectively, are coordinated to the metal center) reveal that the spectrum of $Cu^{II}DTPA{\cdot}H^{2-}$ corresponds closely to that of $Cu^{II}HEDTA$ while that for $Cu^{II}DTPA^{3-}$ resembles the $Cu^{II}dien^{2+}$ system.

Therefore, two distinct structures were proposed by Chabarek, *et al.*,[10] for $Cu^{II}DTPA$. In the nonprotonated complex, three nitrogen groups and one carboxylate group of the DTPA molecule are coordinated to the metal center, while the remaining four carboxylates are not coordinated. In the protonated complex, however, only two nitrogens are coordinated, along with two carboxylate groups, and the proton is bonded to the nitrogen of a free iminodiacetate group. These proposed structures are further substantiated by an additional experimental observation.[9-11,14]

It is believed that DTPA complexes of Ni(II) and Co(II), although octahedral, undergo the same type of rearrangements upon protonation. In the nonprotonated form of Co(II) complex, for example, three nitrogens and three carboxylate groups would be bound to the central metal ion, shown as A_b in Figure 1. Protonation of this complex would occur at a terminal nitrogen, resulting in the formation of a free iminodiacetate group. Only two nitrogens along with three carboxylate groups would be coordinated to the cobalt, with water occupying the sixth coordination position (A_a in Figure 1).

The existence of two forms of the DTPA complex of Co(II) in equilibrium with each other, with an acid dissociation constant of about 5, offers a reasonable explanation for the strong acid dependence of our slow reaction in the pH range of 5–7. Since both the pentadentate, A_a, and the hexadentate, A_b, species are basically Co^{II}(chelate) complexes, like $Co^{II}EDTA$ or $Co^{II}CyDTA$, with the only difference being the structure of the chelate group, there is no reason to believe that ferricyanide ion should not attack both A_a and A_b in the same manner that the other complexes are attacked. In the attack on A_a, the weakest ligand, H_2O, would be most readily displaced by the entering cyano group, to produce a binuclear intermediate, I_{1a}, as shown in Figure 2. In the I_{1a} molecule, the cobalt center would be coordinated to only two nitrogen atoms, just as in the A_a molecule. Cyano group attack on A_b, however, must be accompanied by displacement of one of the bound acetate groups, just as with $Co^{II}EDTA$, thereby resulting in an intermediate, I_{1b} in which the cobalt center is 3*N*-coordinated.

The intermediate I_{1b} would be expected to decompose to

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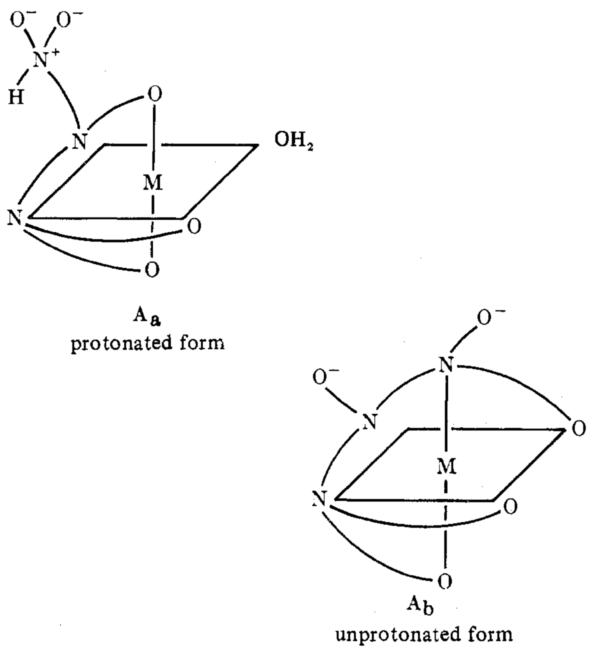

Figure 1. Structural forms for M-DTPA complexes.

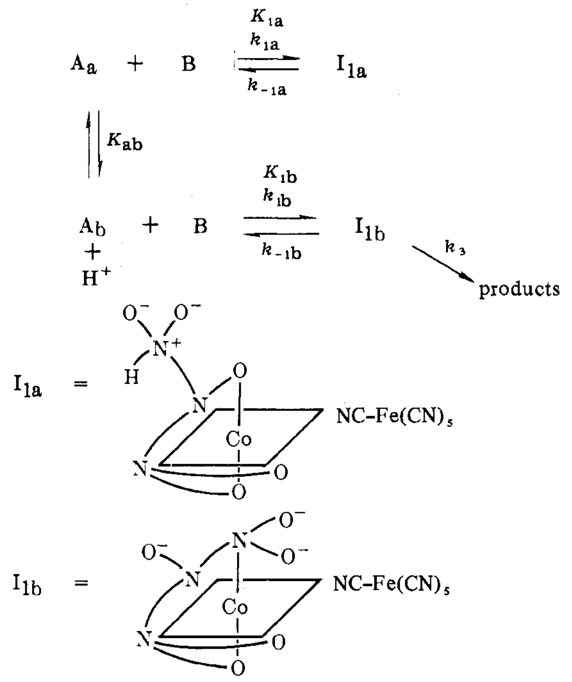

Figure 2. Proposed mechanism for the reaction of $Co^{II}DTPA$ (A_a + A_b) with $Fe(CN)_6{}^{3-}$ (B).

products in a similar fashion to the EDTA and CyDTA reactions, but I_{1a} for reasons to be discussed later, should decompose only very slowly if at all. For the present, the hypothesis is made, subject to later discussion, that I_{1a} does not decompose to products. It is then possible to derive a rate law for the I_{1b} decomposition step.

The proposed mechanism, in which $Co^{II}DTPA$ in a pentadentate structure, A_a, and in a hexadentate form, A_b, each react rapidly to form intermediates I_{1a} and I_{1b}, respectively, with $Fe(CN)_6{}^{3-}$, can be represented as shown in Figure 2, where $Fe(CN)_6{}^{3-}$ = B and K_{1a} and K_{1b} are equilibrium constants. The two forms of $Co^{II}DTPA$ attain equilibrium with an acid dissociation constant K_{ab}.

The rate decomposition of I_{1b} to products can be written

$$\text{rate} = k_3[I_{1b}]$$

The total concentration of $Fe(CN)_6{}^{3-}$ at the beginning of the reaction exists in three forms, following establishment of the rapid equilibria; *i.e.*

$$[B_{tot}] = [B] + [I_{1a}] + [I_{1b}]$$

The concentration of the reacting species I_{1b} for the reaction under consideration is controlled by the concentrations of the other species B and I_{1a}, with which it is in equilibrium. Consequently one must consider the concentration of B_{tot} at any time during the reaction. Following the procedure presented earlier[1] and taking into account both forms of Co^{II}-DTPA and both forms of the intermediate one obtains the expression

$$\frac{1}{k_{3\text{app}}} = \frac{1}{k_3} + \frac{1}{k_3K_{1b}[A_b]} + \frac{K_{1a}[A_a]}{k_3K_{1b}[A_b]}$$

or in terms of $[A_{total}]$

$$\frac{1}{k_{3\text{app}}} = \frac{1}{k_3} + \frac{1 + [H^+]/K_{ab}}{k_3K_{1b}[A_{tot}]} + \frac{k_{1a}[H^+]}{k_3K_{1b}K_{ab}}$$

This rate expression, derived in full in the Appendix, indicates that the reciprocal apparent rate constant, $k_{3\text{app}}{}^{-1}$ should be linearly dependent on the reciprocal total concentration of $Co^{II}DTPA$ complex, $[A_{tot}]^{-1}$ when a series of rate measurements is carried out at constant pH and when $Co^{II}DTPA$ is present in large excess over $Fe(CN)_6{}^{3-}$. Furthermore, for a series of rate measurements conducted at different acid concentrations with $[Co^{II}DTPA]$ being held constant, $k_{3\text{app}}{}^{-1}$ should be linearly dependent on $[H^+]$.

Both these types of measurements have been carried out at each of four temperatures between 30 and 45°. The results are reported in Tables I and II. It is found that the data are indeed linear when plotted in the above manner, as shown in Figures 3 and 4. Thus, in all respects the experimental data conform to the derived rate expression.

Inspection of the rate expression above shows that the plot of $k_{3\text{app}}{}^{-1}$ *vs.* $[A_{tot}]^{-1}$ has a slope and intercept

$$\text{slope} \equiv S_1 = \frac{1}{k_3K_{1b}}\left(1 + \frac{[H^+]}{K_{ab}}\right)$$

$$\text{intercept} \equiv I_1 = \frac{1}{k_3}\left(1 + \frac{K_{1a}[H^+]}{K_{1b}K_{ab}}\right)$$

The plot of $k_{3\text{app}}{}^{-1}$ *vs.* $[H^+]$, on the other hand, has a slope and intercept

$$\text{slope} \equiv S_2 = \frac{1}{k_3K_{1b}K_{ab}}\left(\frac{1}{[A_{tot}]} + K_{1a}\right)$$

$$\text{intercept} \equiv I_2 = \frac{1}{k_3}\left(1 + \frac{1}{K_{1b}[A_{tot}]}\right)$$

Thus, one has experimental values for the four expressions, S_1, I_1, S_2, and I_2, in the four unknowns, k_3, K_{1a}, K_{1b}, and K_{ab}. In principle it is possible to solve for all four unknowns. In actual practice, however, it is found that the expression obtained on simultaneous solution of the four equations involves terms containing small differences between large numbers. This fact, together with the experimental error of the measurements, precludes obtaining all four unknown parameters from the data. This presents no serious problems, how-

Table I. Apparent Rate Constants as a Function of Concentration for the Decomposition of (DTPA)Co^{III}-NC-$Fe^{II}(CN)_5$ to Products[a]

Temp, °C	pH	$10^2[Co^{II}DTPA]$, *M*	10^4k_{3app},[b] sec^{-1}
30.00	5.000 ± 0.002	0.850	2.22
		1.00	2.38
		1.20	2.55
		1.50	2.68
		1.50	2.68
		2.00	2.92
		2.50	3.05
		2.50	2.99
		3.00	3.06
35.00	6.007 ± 0.002	1.00	7.84
		1.20	8.88
		1.30	9.24
		1.50	10.1
		1.70	11.2
40.00	6.017 ± 0.002	0.650	6.46
		0.700	6.64
		1.00	9.03
		1.20	10.4
		1.50	12.6
		1.70	14.2
45.00	6.027 ± 0.002	0.700	8.43
		0.800	10.1
		1.00	11.5
		1.50	17.5

[a] $[Fe(CN)_6^{3-}]_0 = 3.00 \times 10^{-4}$ *M* for the measurements at 30° and 2.00×10^{-4} *M* for the measurements at the higher temperatures. $\mu = 0.660$ in all cases. [b] Observed first-order rate constant.

Table II. Apparent Rate Constants as a Function of $[H^+]$ for the Decomposition of (DTPA)Co^{III}-NC-$Fe(CN)_5$ to Products[a]

Temp, °C	$10^2[Co^{II}DTPA]$, *M*	$[H^+]$, *M*	10^4k_{3app},[b] sec^{-1}
30.00	2.50	5.15×10^{-5}	0.907
		3.09×10^{-5}	1.34
		1.00×10^{-5}	2.99
		1.00×10^{-5}	3.05
		1.61×10^{-6}	8.60
		1.00×10^{-7}	12.6
		1.00×10^{-8}	12.8
35.00	1.50	3.11×10^{-5}	2.13
		1.96×10^{-5}	3.06
		9.84×10^{-6}	4.66
		3.92×10^{-6}	7.06
		9.84×10^{-7}	10.1
40.00	1.50	3.04×10^{-5}	3.80
		1.92×10^{-5}	5.53
		9.62×10^{-6}	7.60
		3.83×10^{-6}	10.1
		9.62×10^{-7}	12.6
		9.62×10^{-8}	13.4
45.00	1.50	2.97×10^{-5}	5.97
		1.87×10^{-5}	7.93
		9.40×10^{-6}	10.9
		3.74×10^{-6}	15.0
		9.40×10^{-7}	17.5

[a] $[Fe(CN)_6^{3-}] = 3.00 \times 10^{-4}$ *M* for the measurements at 30° and 2.00×10^{-4} *M* for the measurements at the higher temperatures. $\mu = 0.660$ in all cases. [b] Observed first-order rate constant.

Table III. Derived Parameters for the Interaction between $Co^{II}DTPA$ and $Fe(CN)_6^{3-}$

Temp, °C	10^3k_3, sec^{-1}	K_{1b}, M^{-1}
30.00 ± 0.01	1.35 ± 0.28	112 ± 20
35.00 ± 0.01	2.41 ± 0.04	51 ± 9
40.00 ± 0.01	3.99 ± 0.44	34 ± 6
45.00 ± 0.01	6.68 ± 1.53	26 ± 11

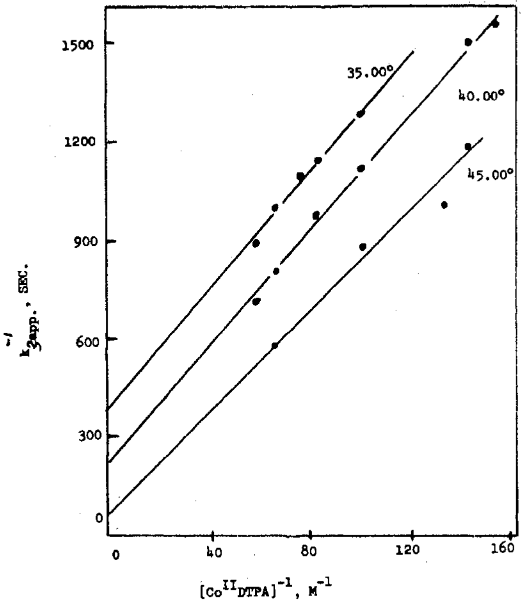

Figure 3. Double-reciprocal plot for decomposition of (DTPA)-Co^{III}-NC-$Fe^{II}(CN)_5$ (pH 6.0).

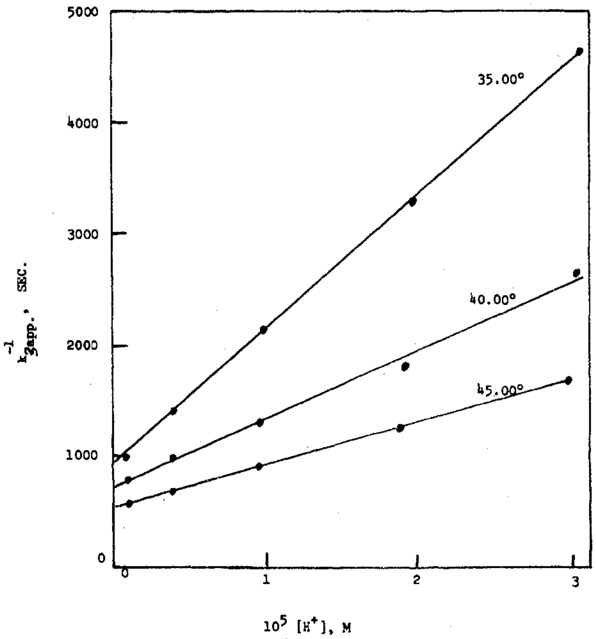

Figure 4. k_{3app}^{-1} *vs.* $[H^+]$ for decomposition of (DTPA)Co^{III}-NC-$Fe^{II}(CN)_5$ ($[A_{tot}]_0 = 0.015$ *M*).

ever, since values of K_{ab} have been reported in the literature. Taking the mean of the two values reported[9,11] at 20° together with the value at 25°[10] and correcting for the differences in temperature, values of K_{ab} are obtained which then permit the quantities k_3, K_{2b}, and K_{1b} to be evaluated.

The results of this calculation are listed in Table III for k_3 and K_{1b} along with the error limits for each value calculated from the standard errors of the slopes and intercepts which were obtained from the experimental data by means of a linear regression program.

An Eyring plot of ln (k_3/T) *vs.* $1/T$ was constructed from the experimental rate constant and the corrected temperatures. Experimental values for the activation parameters obtained from this plot are $\Delta H_3^* = 19.7 \pm 0.4$ kcal/mol and $\Delta S_3^* = -6.7 \pm 1.2$ cal/deg mol. The value of the enthalpy of reaction for the preequilibrium step ($\Delta H_{1b}°$) is -18.3 ± 2.9 kcal/mol.

A value of $K_{1a} = 184 \pm 95$ M^{-1} is obtained from the calculations at 30°. The rather large error limits are a consequence of the fact that, unlike the other parameters, the calculation of K_{1a} involves a substantial accumulation of errors, since

$$K_{1a} = k_3 K_{1b} K_{ab} S_2 - \frac{1}{[A_{tot}]}$$

In this expression, only the last term is known with certainty. Each of the other four terms contains errors which are reflected in K_{1a}. At the three higher temperatures the errors are so large that reasonable values of K_{1a} cannot be obtained.

Formation of I_{1b}. Measurements of the kinetics of formation of the intermediate for the DTPA system were carried out at 30° on the stopped-flow apparatus. In each case the ionic strength was maintained at $\mu = 0.660$ with sodium acetate and the pH was adjusted to 5.00 with acetic acid. The reaction was found to follow first-order kinetics when Co^{II}DTPA was present in excess over $Fe(CN)_6{}^{3-}$. Mean values of the apparent rate constants together with the standard errors of the mean are listed in Table IV. The rate expression used to calculate the true second-order rate constants reported in column 6 of Table IV is identical with that derived for the Co^{II}CyDTA system[3]

$$k_{1b} = \frac{k_{1app}}{[A_b] + K_{1b}{}^{-1}}$$

where $K_{1b} = 112\ M^{-1}$ at 30° and $[A_b]$ is calculated from the known values of pK_{ab},[9-11] adjusted to a temperature of 30°.

Both the protonated and the unprotonated forms of the DTPA complex of cobalt(II), *i.e.*, A_a and A_b as shown in Figure 1, exist in solution at pH 5. Both forms would be subject to nucleophilic attack by $Fe(CN)_6{}^{3-}$. It should be expected, however, that the protonated, pentadentate form, A_a, would react much more rapidly with $Fe(CN)_6{}^{3-}$ than the hexadentate form, A_b. In the former case, the most weakly bound ligand, water, would be displaced by the incoming cyano bridging ligand, while in the latter case, a bound chelate acetate must be displaced, which should occur more slowly.

Direct evidence of this has also been obtained by means of a few stopped-flow measurements on the reaction of Co^{II}HEDTA (HEDTA = *N*-hydroxyethylethylenediaminetriacetic acid) with $Fe(CN)_6{}^{3-}$. In this complex, the ligand is completely pentadentate at pH 5, with water occupying the sixth coordination site. This reaction qualitatively follows the same reaction scheme as the others, in that a deeply colored intermediate rapidly forms and then slowly decomposes to give Co^{III}HEDTA and $Fe(CN)_6{}^{4-}$ products. The decomposition step is quite slow at room temperature and the conversion from reactants to intermediate is large. Therefore, the magnitude of the equilibrium constant K_1 was readily determined spectrophotometrically to be ~5000 M^{-1} at room temperature.

Stopped-flow measurements on this system under the conditions of pH 5.00 and $\mu = 0.660$ revealed that the rate constant for formation of the intermediate is $k_{1app} \approx 2 \times 10^2$ sec^{-1}, when $[Co^{II}HEDTA]_0 = 2 \times 10^{-3}\ M$. Since

$$k_1 = \frac{k_{1app}}{[A] + K_1^{-1}}$$

as before, a value of $k_1 \approx 10^5\ M^{-1}\ sec^{-1}$ can be calculated.

This value may be considered to be a lower limit for the rate constant k_{1a} for the corresponding reaction of Co^{II}DTPA·H, in which the chelate ligand is also pentadentate. By comparison of this value with that of $k_{1b} = 1.5 \times 10^4\ M^{-1}\ sec^{-1}$, it can be seen that $k_{1a} > 6.6 k_{1b}$. In other words, by the time 1 half-life has elapsed in the formation of I_{1b}, the formation of I_{1a} is >99% complete. It may be noted here that approximately 1 half-life is obscured in the formation of I_{1b} because of the dead time of the instrument. Thus it may be concluded that the experimental values of k_{1b} are not complicated by any observable contribution due to the formation of I_{1a}.

Table IV. Rate Data[a] for the Formation of I_{1b} from Co^{II}DTPA + $Fe(CN)_6{}^{3-}$

$10^3[A_{tot}]$, *M*	$10^4[Fe(CN)_6{}^{3-}]$, *M*	No. of replicates	k_{1app}, sec^{-1}	$10^{-4}k_{1b}$, $M^{-1}\ sec^{-1}$
5.00	3.00	3	213 ± 4	1.90 ± 0.03
5.00	3.00	10	213 ± 7	1.90 ± 0.07[b]
7.50	4.00	4	190 ± 14	1.54 ± 0.12
12.5	4.00	3	224 ± 7	1.54 ± 0.05

[a] Temperature 30°, pH 5.000 ± 0.002, $\mu = 0.660$, $[A_{tot}] = [Co^{II}DTPA] + [Co^{II}DTPA{\cdot}H]$. [b] Both component solutions, stopped-flow storage cylinders and mixing chamber flushed with argon for 1.5 hr prior to measurements.

Table V. Comparison of Results at 30°

	Co^{II}EDTA[a]	Co^{II}DTPA[c]	Co^{II}CyDTA[a]
k_1, $M^{-1}\ sec^{-1}$	7×10^4 [b]	1.5×10^4	3.9×10^3
K_1, M^{-1}	501	112	26.2
$\Delta H_1°$, kcal mol^{-1}	−16.7	−18.3	−17.5
k_3, sec^{-1}	11.2×10^{-3}	1.35×10^{-3}	43.2×10^{-3}
ΔH_3, kcal mol^{-1}	+25.4	+19.7	+23.0
ΔS_3, cal $deg^{-1}\ mol^{-1}$	+16.1	−6.7	+10.9

[a] Reference 3. [b] Reference 2. [c] For the hexadentate form.

Comparison of Co^{II}(chelate) Systems. A summary and comparison of rate constants, equilibrium constants, and associated thermodynamic parameters are presented for the Co^{II}EDTA, Co^{II}CyDTA, and Co^{II}DTPA systems (at 30°) in Table V.

Inspection of Table V shows that k_{1b} for the DTPA reaction is smaller than k_1 for the EDTA reaction and larger than k_1 for the reaction involving the CyDTA complex. We can address ourselves to these differences in terms of steric considerations. Molecular models show that it is more difficult for an acetate group to move away from the bridging position in the hexadentate DTPA complex than in the EDTA complex due to steric interaction of both the methylene protons and the carboxyl group with neighboring ligands in the complex. Once the displaced acetate is able to find its way out, however, it is not constrained to a position close to the bridging site as in the case of the CyDTA complex; thus explaining the faster rate of the former. Values of K_1 reflect the corresponding k_1 values.

The value of k_3 at 30° for the DTPA system is $^1/_8$th as large as for the EDTA intermediate and less than $^1/_{30}$th as large as the rate for the CyDTA case. While steric constraint to keep the displaced acetate near the cyano group was responsible for the larger rate constant with CyDTA, it is probable that steric hindrance between adjacent ligand groups preventing the entry of a ligand acetate into the inner coordination sphere of the DTPA intermediate to displace the bridging cyano group is responsible for the low observed rate of this reaction. The negative entropy of activation for the DTPA reaction appears to be the main cause of the low observed rate constant and can be attributed to the low probability of the free acetate group penetrating the steric restraints and forming a partial bond with the cobalt center in the transition state.

Registry No. A_a, 38531-77-0; A_b, 38560-57-5; I_{1a}, 38531-81-6; I_{1b}, 38531-82-7; $Fe(CN)_6{}^{3-}$, 13408-62-3.

Appendix

Derivation of the Rate Expression for the Slow Reaction. The rate of decomposition of I_{1b}

$$\text{rate} = k_3[I_{1b}] \qquad (1)$$

must be rewritten in terms of B_{tot}, B, and I_a (*vide infra*) since

$$[I_{1b}] = [B_{tot}] - [B] - [I_{1a}]$$

and

$$K_{1a} = [I_{1a}]/[A_a][B]$$

The substitution can be made as in

$$[I_{1b}] = [B_{tot}] - [B]\{(1 + K_{1a}[A_a])\} \qquad (2)$$

Then since

$$K_{1b} = [I_{1b}]/[A_b][B]$$

one can solve for [B] and make this substitution in (2)

$$[I_{1b}] = [B_{tot}] - \frac{[I_{1b}](1 + K_{1a}[A_a])}{K_{1b}[A_b]}$$

Gathering like terms, it can be seen that

$$[I_{1b}] = \frac{[B_{tot}]}{1 + \dfrac{1 + K_{1a}[A_a]}{K_{1b}[A_b]}} \qquad (3)$$

Sustituting (3) into the rate expression 1 gives

$$\text{rate} = \frac{k_3}{1 + \dfrac{1 + K_{1a}[A_a]}{K_{1b}[A_b]}}[B_{tot}] = k_{3\text{app}}[B_{tot}] \qquad (4)$$

Expressing the concentrations of A_a and A_b in terms of A_{tot} and the equilibrium constant K_{ab}, one obtains an expression for the desired rate law

$$\frac{1}{k_{3\text{app}}} = \frac{1}{k_3} + \frac{1 + [H^+]/K_{ab}}{k_3K_{1b}[A_{tot}]} + \frac{K_{1a}[H^+]}{k_3K_{1b}K_{ab}} \qquad (5)$$

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Stereoisomers of the Bis(L-hydrogen aspartato)ethylenediamine- and L-Aspartatobis(ethylenediamine)cobalt(III) Complexes

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The bis(L-hydrogen aspartato)ethylenediamine- and L-aspartatobis(ethylenediamine)cobalt(III) complexes have been prepared from the reaction of the *trans*-$CoCl_2(en)_2^+$ complex with L-aspartic acid. The stereoisomers of these complexes have been separated by an ion-exchange chromatographic method. For the bis(L-hydrogen aspartato)ethylenediamine complexes, the six stereoisomers have newly been isolated; they are Λ- and Δ-trans(O), Λ- and Δ-cis(O),cis(N), and Λ- and Δ-trans(N) isomers. On the other hand, two known diastereoisomers have been isolated for the bis(ethylenediamine) complexes. All of the complexes isolated have been characterized by their electronic absorption, circular dichroism, and proton magnetic resonance spectra. The stereoselectivity in these complexes has also been discussed based on the results of formation ratios of the isomers. The pmr studies have been carried out with regard to the signals of the NH_2 protons.

Introduction

There have been a few papers concerning the stereoselectivity in the mixed diamine complexes of cobalt(III) with L-glutamic acid or L-aspartic acid; Gillard and his coworkers[1] have reported that the reaction of L-glutamic acid with the $CoCO_3(en)_2^+$ complex results in kinetically controlled stereoselective formation of the Λ-Co(L-glu)$(en)_2^+$ isomer (D(+) isomer in the paper). Very recently, he and his coworkers[2] reinvestigated the same reaction in detail, and they have found that the end products in this reaction are not only the paired isomers (Λ and Δ) of that bis(ethylenediamine) complex but also a racemic mixture of another type of bis(ethylenediamine) complex. They believed the latter to be the complex with the L-glutamate ligand bound through two carboxyl groups. Legg and Steele[3] have isolated several pairs of the Co(L-aa)$(en)_2^+$ and Co(L-Haa)$(en)_2^{2+}$ complexes (aa = aspartate and glutamate, Haa = protonated aspartate and glutamate) from the reaction of the amino acid with the $CoCO_3(en)_2^+$ in the presence of activated charcoal. They have found a 70:30 distribution between the Λ and Δ isomers for the L-glutamato complex, and a 60:40 distribution for the L-aspartato complex. The present authors[4] have also isolated a number of stereoisomers of the Co(L-Hasp)$_2$(*l*-pn)$^+$ and Co(L-asp)(*l*-pn)$_2^+$ complexes and have discussed the stereoselectivity found in terms of the dangling β-carboxylate group in the chelated L-aspartate and the fixed conformation of the chelated *l*-propylenediamine.

The present work has been undertaken in connection with that previous work in order to confirm the stereoselective effect caused by the chelated L-aspartate, since the conformational effect caused by a chelated diamine may well be ignored in the complexes of the ethylenediamine-L-aspartato series. The isolated complexes have been characterized by electronic absorption, circular dichroism (CD), and proton magnetic resonance (pmr) spectra. The description of the work concerning the bis(ethylenediamine) complex will be minimized, since similar work has been published.[3]

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