vent led, in addition to $Pt(\pi\text{-}C_4H_7)ClQ_2$ expected from a cationic mechanism involving *trans*-$[PtCH_3(\pi\text{-allene})Q_2]^+$, to the neutral vinyl ether complex *trans*-$PtCl(C(CH_3){=}CH(OCH_3))Q_2$.[66]

It is interesting at this point to compare the reactivities of $[CH_3PtQ_2]^+$ and $[HPtQ_2]^+$ cations. First, the hydride cations $[HPtQ_2]^+$ are the more reactive toward insertion reactions. This may be partly attributable to the thermodynamic properties of the Pt-H bond compared with those of the Pt-C bond either in the $[CH_3PtQ_2]^+$ cation or in the products. Second, the difference in reactivity may relate to the availability of alternative reaction mechanisms. Thus reactions involving $[CH_3PtQ_2]^+$ proceed in a Markownikov manner by electrophilic attack of Pt^+; for example, as mentioned above, $[Pt(h^3\text{-2-methallyl})Q_2]^+$ is formed from reaction of allene with *trans*-$[PtCH_3(acetone)Q_2]^+$ whereas the analogous 1,3-butadiene cation does not lead to a π-allylic derivative by $Pt{-}CH_3$ insertion. In contrast, $[MPtQ_2]^+$ can react by either a Markownikov or an anti-Markownikov mechanism, *i.e.* Pt^+ or H^+ attack of the unsaturated ligand.[67] A consequence of this apparent versatility is the formation of π-allylic complexes from both allenes and 1,3-dienes with $[HptQ]^+$; moreover, this versatility is responsible for the characteristic isomerization and H-D exchange reactions of olefins with platinum hydrides.[67]

Experimental Methods

General methods have been outlined previously.[17]

The general procedure for the preparation of *trans*-$[PtCH_3(un)Q_2]PF_6$ from *trans*-$[PtCH_3(acetone)Q_2]PF_6$ and un parallels the previous preparation[16] of cationic acetylenic complexes, I, and needs no further comment, save to emphasize the advantage of working in a "noncoordinating" solvent such as methylene dichloride.[21] *trans*-$[PtCH_3(acetone)Q_2]PF_6$ was prepared by the previously described method.[19] Gaseous olefins, dienes, vinyl ethers, and allene were obtained from Matheson; other unsaturated ligands were from the Aldrich Chemical Co. Ltd. and were used without further purification. Purification of the complexes reported here, by short column chromatography and repeated recrystallization, follows that reported for the preparation of I.

The low solubility of $[PtCH_3(CH_2{=}CHCH_2NHCOCH_3)Q]PF_6$ allowed easy separation from the more soluble $[PtCH_3Q_2]PF_6$ in the reaction of allylacetamide with *trans*-$[PtCH_3(acetone)Q_2]PF_6$.

Registry No. *trans*-$[PtCH_3(CH_3COCH_3)Q_2]PF_6$, 36523-59-8; *trans*-$[PtCH_3(CH_3COCH_3)A_2]PF_6$, 38466-92-1; *trans*-$[PtCH_3(CH_2{=}CH_2)Q_2]PF_6$, 38466-79-4; *trans*-$[PtCH_3(CH_3CH{=}CH_2)Q_2]PF_6$, 38466-80-7; *trans*-$[PtCH_3(CH_2{=}C{=}CH_2)Q_2]PF_6$, 38466-81-8; *cis*-$[Pt(\pi\text{-}C_4H_7)Q_2]PF_6$, 38466-82-9; *cis*-$[Pt(\pi\text{-}C_8H_{15})Q_2]PF_6$, 38466-83-0; *cis*-$[Pt(\pi\text{-}C_4H_7)A_2]PF_6$, 38466-84-1; $[PtCH_3(CH_3CONHCH_2CH{=}CH_2)Q]PF_6$, 38466-85-2; *trans*-$[PtCH_3(CH_2{=}CHCH{=}CH_2)Q_2]PF_6$, 38466-86-3; *trans*-$[PtCH_3(CH_2{=}CHOCH_3)Q_2]PF_6$, 36548-52-4; *trans*-$[PtCH_3(CH_2{=}CHOC_2H_5)Q_2]PF_6$, 38466-88-5; *trans*-$[PtCH_3(CH_2{=}CHCH_2OH)Q_2]PF_6$, 38466-89-6; *trans*-$[PtCH_3(CH_2{=}CHCH_2NH_2)Q_2]PF_6$, 38585-01-2; $[Pt(\pi\text{-}C_5H_5)Q_2]PF_6$, 38466-90-9; *trans*-$[PtCH_3(OHCNMe_2)Q_2]PF_6$, 38466-93-2.

Acknowledgments. We are grateful to the National Research Council of Canada for financial support.

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Contribution from the Department of Chemistry,
Seton Hall University, South Orange, New Jersey 07079

Interaction of Multidentate Cobalt(II)-Chelate Complexes with Ferricyanide Ion.[1] I. $Co^{II}EDTA$ and $Co^{II}CyDTA$

DANIEL H. HUCHITAL* and ROBERT J. HODGES

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A cyanide-bridged intermediate is formed between $CoCyDTA^{2-}$ and $Fe(CN)_6{}^{3-}$ in a manner exactly analogous to that for the $CoEDTA^{2-}$-$Fe(CN)_6{}^{3-}$ reaction

$$CoY^{2-} + Fe(CN)_6{}^{3-} \underset{}{\overset{K_1}{\rightleftharpoons}} [Y{-}Co^{III}{-}CN{-}Fe^{II}(CN)_5]^{5-} \xrightarrow{k_3} CoY^- + Fe(CN)_6{}^{4-}$$

The values of K_1, k_1, and k_3 at 25° (pH 5.00, $I = 0.66\ M$ with acetate, acetic acid) are 831 M^{-1}, $8 \times 10^4\ M^{-1}\ sec^{-1}$, and $5.40 \times 10^{-3}\ sec^{-1}$ for $CoEDTA^{2-}$ and 43.6 M^{-1}, $3.58 \times 10^3\ M^{-1}\ sec^{-1}$, and $2.21 \times 10^{-2}\ sec^{-1}$ for $CoCyDTA^-$. Activation parameters are reported. The rate and equilibria data are readily understood on the basis of the steric hindrance suffered by the pendant acetate group in moving aside to allow the entry of the cyano group into the inner coordination sphere of the cobalt complex.

Mechanisms of electron-transfer reactions between inorganic complex ions in solution encompass a substantial segment of current research activity. Of particular interest has been the inner-sphere mechanism[2] in which the transfer of an electron is an intramolecular event. Of the wide variety of inorganic and organic ligands used, the cyano group provides an interesting example of a bridging ligand since it offers the opportunity for simultaneous carbon bonding to one metal ion and nitrogen bonding to the other. A number of inner-sphere reactions involving cyano bridging have been reported in the literature.[3] In reactions of this type, when at least one of the product ions is substitution labile, the decomposition (or dissociation) of the successor binuclear complex is rapid, and conclusions concerning the structure and reactiv-

(1) Presented in part before the Division of Inorganic Chemistry, Symposium on Multistep Redox Reaction Mechanisms, Second Northeast Regional Meeting of the American Chemical Society, Providence, R. I., Oct 1970.

(2) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970.

(3) H. Taube and H. Meyers, *J. Amer. Chem. Soc.*, 76, 2103 (1954); J. H. Espenson and J. P. Birk, *ibid.*, 87, 3280 (1965); J. Halpern and S. Nakamura, *ibid.*, 87, 3002 (1965).

ity of that species must be drawn from indirect evidence.[4] Alternatively, when both product ions are substitution inert, the cyano-bridged species can be extremely stable. Examples are the $Fe(CN)_6{}^{3-}$ oxidations of Cr^{2+} and $Co(CN)_5{}^{3-}$.[5,6] Between these two extreme situations, in one case where the breakdown of the binuclear species is rapid and in the other case where breakdown does not occur, is a third situation in which the bridged complex decomposes slowly. Such a case is of considerable interest since the intermediate (binuclear complex) remains in solution long enough to be examined and also provides the opportunity conveniently to study the kinetics and mechanisms of its decomposition, thereby providing further insight into the nature of this type of complex. This situation is obtained when an inner-sphere redox reaction occurs between two complexes in which both product metal centers are substitution inert and in addition one of the metal ions is complexed with a multidentate ligand. The first example of this type of reaction was reported in 1963 by Adamson and Gonick,[7] who oxidized ethylenediaminetetraacetatocobaltate(II), CoEDTA, with ferricyanide ion.

We have found that a cyano-bridged intermediate is formed between *trans*-1,2-cyclohexanediaminetetraacetatocobaltate(II), CoCyDTA, and ferricyanide ion in a manner exactly analogous to that for the $CoEDTA^{2-}$-$Fe(CN)_6{}^{3-}$ reaction. CyDTA was chosen because the stereochemistry of the cyclohexyl ring plays an important part in reactions of complexes of this ligand.[8]

Experimental Section

Materials. Each of the ligands was checked for purity by titration against a standard zinc solution (zinc foil, 99.99%) at pH 5 using Xylenol Orange as an indicator. The EDTA, in the disodium form, and the CyDTA, in the acid form, were found to have purities of 99.70 and 99.37%, respectively. All other chemicals used were of reagent grade quality. Standard solutions were prepared by weight in all cases except cobalt(II) nitrate which was standardized by titration with EDTA.

Apparatus. Kinetic measurements were carried out on a Cary 15 spectrophotometer (slow runs) equipped with a water-jacketed cell holder and an Aminco-Morrow stopped-flow apparatus (American Instrument Co., Silver Springs, Md.). Spectra were obtained with a Beckman DK-2 spectrophotometer at 2.46°. The pH values of the reaction solutions were determined using a Radiometer Model PHM 4c pH meter.

Solution Preparation. All solutions were prepared to be at ionic strength, $\mu = 0.660$ and pH 5.00 using sodium acetate and acetic acid as buffer components. The final pH was adjusted by adding either acetic acid or sodium hydroxide. A 10% excess of ligand over cobalt(II) nitrate was used in all runs. All solutions were prepared the same day as measurements were made.

Kinetics Measurements. The kinetics of the decomposition of the intermediate were carried out under pseudo-first-order conditions with Co^{II}(chelate) in large excess over $Fe(CN)_6{}^{3-}$. Temperature variation during the course of the reaction was found to be a major source of error as this shifts the rapid equilibrium between reactants and intermediate which in turn alters the rate of reaction. Therefore, reactions were carried out in 10-cm quartz absorption cells with narrow openings into which a thermometer was inserted at frequent intervals during each run. Temperatures reported are mean values.

The reactions were followed at 420 nm. Rate constants were obtained from slopes of plots of log $(A_t - A_\infty)$ *vs.* time where A_t and A_∞ are the absorbances at time *t* and after the reaction is complete.

The rate of formation of the intermediate from Co^{II}(chelate) and $Fe(CN)_6{}^{3-}$ was studied under second-order (equal concentrations) as well as pseudo-first-order conditions when permissible. The conditions for these stopped-flow runs were the same as for the slow decomposition studies.

Spectrophotometry. The spectrum of the intermediate, I_1, for the $Co^{II}CyDTA + Fe(CN)_6{}^{3-}$ system was determined at 2.46° as the per cent conversion to I_1 is increased at low temperatures and the rate of decomposition of I_1 is reduced. However, due to the concentration conditions dictated for reasonable absorption data to be obtained ($[CoCyDTA^{2-}] = 1.00 \times 10^{-2}$ *M*, $[Fe(CN)_6{}^{3-}] = 1.3 \times 10^{-4}$ *M*), the conversion to I_1 is only approximately 85%. In addition, the decomposition still occurs at a measurable rate. Both these facts must be accounted for. Thus, the spectrum of I_1 was determined by a modified Rose-Drago method[9] as follows.

A 5-cm sample cell was filled with a solution of $Co^{II}CyDTA$ containing 10% excess ligand, sodium acetate, and acetic acid ($\mu = 0.660$; pH 5.00). A matched 5-cm reference cell was filled with a solution containing the same concentrations of sodium acetate and acetic acid as the sample solution, as well as [CyDTA] equal to the concentration of excess ligand in the sample solution. Both cells were purged with argon, placed in the DK-2 spectrophotometer, and cooled to 2.46°. Two additional solutions, one containing both $Fe(CN)_6{}^{3-}$ and $Fe(CN)_6{}^{4-}$ and the other $Fe(CN)_6{}^{4-}$ only, were also prepared. Aliquots of these solutions were then quickly injected into the two cells using standard anaerobic syringe techniques, so that concentrations of 1.30×10^{-4} *M* $Fe(CN)_6{}^{3-}$ in the sample cell and 1.00×10^{-2} *M* $Fe(CN)_6{}^{4-}$ in both cells are obtained. The purpose of the ferrocyanide is to suppress the tendency of I_1 to become oxidized to I_2, $[CyDTACo^{III}\text{-}NC\text{-}Fe^{III}(CN)_5]^{4-}$, by residual ferricyanide ion.

Complete spectra were then repeatedly recorded over the visible range and the elapsed time marked on the curves. Absorbances were found to decrease with time at all wavelengths due to the slow decomposition of I_1 to products. Absorbances corresponding to the situation prior to any decomposition of I_1 are obtained by constructing a first-order plot of log $(A_t - A_\infty)$ *vs.* time and extrapolating back to zero time. For this purpose, values of A_∞ are obtained from the absorbance data by the Mangelsdorf method.[10] This procedure is carried out at each of 20 wavelengths in the visible region.

The entire process was then repeated for two other concentrations of $Co^{II}CyDTA$, the concentrations of $Fe(CN)_6{}^{3-}$ and $Fe(CN)_6{}^{4-}$ being held constant. The three spectra thereby obtained represent the total absorbance of the three components $Co^{II}CyDTA$, $Fe(CN)_6{}^{3-}$, and I_1. The proportions of the three components are controlled by the magnitude of the equilibrium constant, K_1 at 2.46°.

Our modified Rose-Drago method was then used to calculate the extinction coefficient of the intermediate at each wavelength by solving the quadratic equation

$$\Delta\epsilon = \frac{\Delta Q \pm [(\Delta Q)^2 - 4\Delta Z \Delta W]^{1/2}}{2\Delta Z}$$

where

$$\Delta\epsilon = \epsilon_{I_1} - \epsilon_{Co^{II}CyDTA} - \epsilon_{Fe(CN)_6{}^{3-}}$$

and ΔQ, ΔW, and ΔZ are the differences in these parameters for two solutions

$$Q = [Co^{II}CyDTA]_0 + [Fe(CN)_6{}^{3-}]_0$$

$$W = \frac{A_t}{l} - \epsilon_{Co^{II}CyDTA}[Co^{II}CyDTA]_0 - \epsilon_{Fe(CN)_6{}^{3-}}[Fe(CN)_6{}^{3-}]_0$$

$$Z = \frac{[Co^{II}CyDTA][Fe(CN)_6{}^{3-}]}{W}$$

where A_t is the total absorbance and *l* is the path length.

The spectrum obtained is shown in Figure 1. Calculation of the degree of conversion of reactants to I_1 and of the equilibrium constant K_1 was carried out at 14 wavelengths between 500 and 640 nm. The

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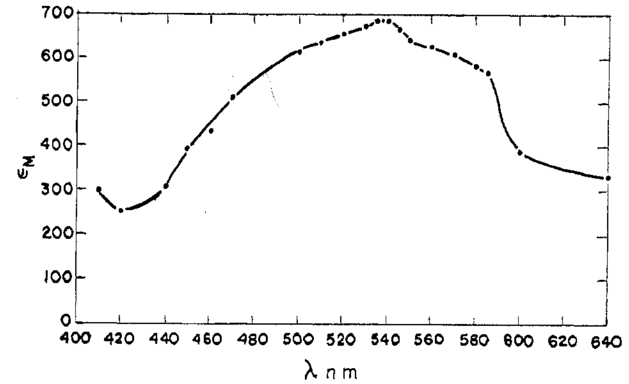

Figure 1. Spectrum of (CyDTA)Co^{III}-NC-$Fe^{II}(CN)_5{}^{5-}$.

mean value and standard error of the mean for 42 calculations is $K_1 = 528 \pm 127\ M^{-1}$.

Results

Rate Data. $Co^{II}EDTA + Fe(CN)_6{}^{3-}$. Kinetic measurements previously reported[7] for the decomposition of the intermediate to products were limited to 25° except for some crude data at 5°. These measurements were repeated and additional experiments were carried out at 15, 20, and 30°. Reactions were carried out under conditions where [Co^{II}EDTA] was in large excess. The absorbance data at 420 nm obeyed a first-order kinetic scheme when log $(A_t - A_\infty)$ was plotted against time. The results of the measurements are reported in Table I in which $k_{3\mathrm{app}}$ in the observed first-order rate constant obtained from the slope of the kinetics plot.

The results are reported and discussed in accordance with the reaction scheme presented in the literature,[11] *viz.*

$$Co^{II}(\text{chelate}) + Fe(CN)_6{}^{3-} \rightleftharpoons \underset{I_1}{[(\text{chelate})Co^{III}\text{-NC-}Fe^{II}(CN)_5]^{5-}} \qquad k_1, k_{-1}, K_1 \quad (1)$$

$$[(\text{chelate})Co^{III}\text{-NC-}Fe^{II}(CN)_5]^{5-} + Fe(CN)_6{}^{3-} \rightleftharpoons \underset{I_2}{[(\text{chelate})Co^{III}\text{-NC-}Fe^{III}(CN)_5]^{4-}} + Fe(CN)_6{}^{4-} \quad k_2, k_{-2}, K_2 \quad (2)$$

$$[(\text{chelate})Co^{III}\text{-NC-}Fe^{II}(CN)_5]^{5-} \rightarrow Co^{III}(\text{chelate}) + Fe(CN)_6{}^{4-} \qquad k_3 \quad (3)$$

The second reaction can be ignored in the calculations to determine K_1 and k_3 since, even at the lowest Co^{II}(chelate) concentrations used, the buildup of I_2 (the Co^{III}-Fe^{III} binuclear intermediate) never exceeds 10%. Thus, the reaction scheme reduces to steps 1 and 3 for which the observed first-order rate constant ($k_{3\mathrm{app}}$) is[7]

$$k_{3\mathrm{app}} = \frac{k_3K_1[Co^{II}(\text{chelate})]}{1 + K_1[Co^{II}(\text{chelate})]}$$

Taking the reciprocal of both sides

$$\frac{1}{k_{3\mathrm{app}}} = \frac{1}{k_3K_1[Co^{II}(\text{chelate})]} + \frac{1}{k_3}$$

When the experimental values of $k_{3\mathrm{app}}{}^{-1}$ are plotted *vs.* [Co^{II}EDTA]$^{-1}$, linearity is observed at each of the four temperatures. Values of k_3 and K_1, calculated from the intercepts and slopes of these double-reciprocal plots (Figure 2) are listed in Table II. The activation parameters, obtained by a least-squares fit of the rate constants to the Eyring equation, are $\Delta H_3{}^* = 25.4 \pm 0.4$ kcal/mol and $\Delta S_3{}^* = 16.1 \pm 1.4$ cal/deg mol. A value of $\Delta H_1{}^\circ = -16.7 \pm 0.4$ kcal/mol is obtained from the temperature variation of K_1 by the usual procedure.

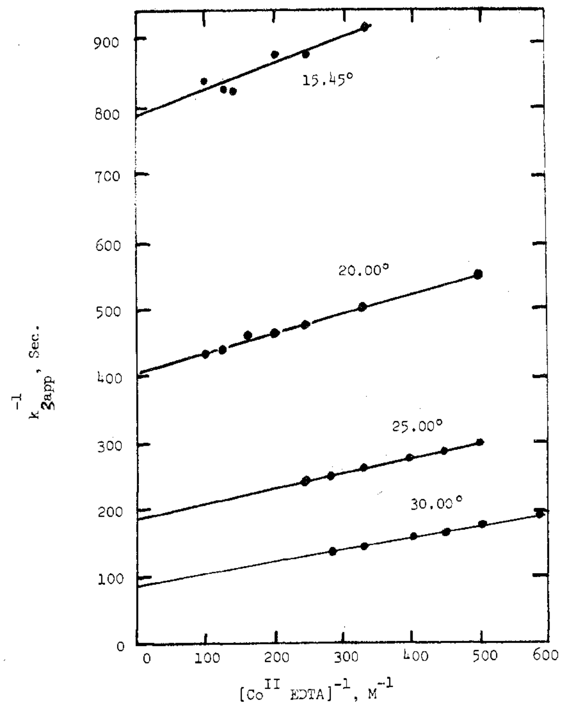

Figure 2. Double-reciprocal plot for the decomposition of I_1 to products for the Co^{II}EDTA system.

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

Temp, °C	$10^3[Co^{II}EDTA]$, M	$10^3k_{3\mathrm{app}}$,[b] $\sec^{-1}$
15.45	3.00	1.10
	4.00	1.14
	5.00	1.15
	7.00	1.21
	8.00	1.21
	10.0	1.20
20.00	2.00	1.82
	3.00	1.98
	4.00	2.10
	5.00	2.17
	6.00	2.18
	8.00	2.30
	10.0	2.33
25.00	2.00	3.35
	2.20	3.50
	2.20	3.50
	2.50	3.65
	3.00	3.85
	3.50	4.00
	4.00	4.16
30.00	1.70	5.20
	2.00	5.58
	2.20	5.85
	2.50	6.17
	3.00	6.83
	3.50	7.08

[a] $[Fe(CN)_6{}^{3-}] = 1.00 \times 10^{-4}\ M$, $\mu = 0.660$, pH 5.000 ± 0.002.
[b] Observed first-order rate constant.

The data in Table II for 25° may be compared with the corresponding values reported by Adamson and Gonick.[7] Their values of $6.0 \times 10^{-3}\ \sec^{-1}$ (k_3) and $670\ M^{-1}$ (K_1) are in reasonably good agreement with ours considering the limited temperature control of their experiments.

Measurements of the rate of formation of I_1 were carried out at 25° with [Co^{II}EDTA] = $[Fe(CN)_6{}^{3-}] = 2.00 \times 10^{-4}\ M$ (ionic strength 0.66, pH 5.0) The mean half-life for this

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

Co^{II}EDTA

Temp, °C	10^3k_3, sec^{-1}	$10^{-2}K_1$, M^{-1}
15.45 ± 0.01	1.28 ± 0.03	20.4 ± 3.4
20.00 ± 0.01	2.49 ± 0.02	13.3 ± 0.6
25.00 ± 0.02	5.40 ± 0.03	8.31 ± 0.17
30.00 ± 0.02	11.2 ± 0.3	5.01 ± 0.20

Co^{II}CyDTA

Temp, °C	10^3k_3, sec^{-1}	K_1, M^{-1}
17.00 ± 0.01	7.56 ± 0.23	94.4 ± 4.6
20.00 ± 0.01	10.8 ± 0.2	75.0 ± 1.8
25.00 ± 0.01	22.1 ± 0.5	43.6 ± 1.3
30.00 ± 0.01	43.2 ± 1.7	26.2 ± 1.9

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

Temp, °C	10^3[Co^{II}CyDTA], M	10^3k_{3app},[b] sec^{-1}
17.00	2.50	1.44
	3.00	1.67
	4.00	2.10
	5.00	2.45
	7.00	2.96
20.00	2.50	1.71
	3.00	1.98
	4.00	2.50
	5.00	2.94
	7.00	3.72
25.00	1.70	1.53
	2.00	1.77
	2.50	2.17
	3.00	2.56
	5.00	3.96
	7.00	5.04
	10.0	6.89
30.00	1.50	1.60
	2.00	2.13
	2.50	2.69
	3.00	3.16
	4.00	4.13

[a] [$Fe(CN)_6{}^{3-}$] = 1.00 × 10^{-4} M, μ = 0.660, pH 5.000 ± 0.002.
[b] Observed first-order rate constant.

reaction, from a set of five replicates, was 9.1 ± 0.4 msec. This value is in good agreement with the value of 10 msec reported[11] and, thus, no further measurements were carried out with this system.

Co^{II}CyDTA + $Fe(CN)_6{}^{3-}$. Kinetics results for the reaction of $CoCyDTA^{2-}$ with $Fe(CN)_6{}^{3-}$ are reported in Tables II and III. First-order kinetics were obeyed for the slow reaction when $CoCyDTA^{2-}$ was present in large excess ([$CoCyDTA^{2-}$] = 1.00 × 10^{-3} to 1.00 × 10^{-2} M, [$Fe(CN)_6{}^{3-}$] = 1.00 × 10^{-4} M). The values of k_3 and K_1, obtained in the same manner as for the EDTA system (Figure 3), are reported in Table II. The activation parameters $\Delta H_3{}^*$ and $\Delta S_3{}^*$ and the enthalpy of reaction $\Delta H_1{}^\circ$ for the pre-equilibrium step are 23.0 ± 0.7 kcal/mol, 10.9 ± 1.5 cal/deg mol, and −17.5 ± 0.8 kcal/mol, respectively.

Kinetics of the rapid formation of I_1 were studied using the stopped-flow technique at four temperatures from 8.00 to 24.80°. The reactions were run under conditions where the cobalt complex was in large excess. The observed first-order rate constant obtained from kinetic plots was used to obtain the true second-order rate constant by use of the equation

$$k_1 = k_{obsd}/(A + K_1{}^{-1})$$

where A = [$CoCyDTA^{2-}$]. Results of these kinetic measurements are presented in Table IV.

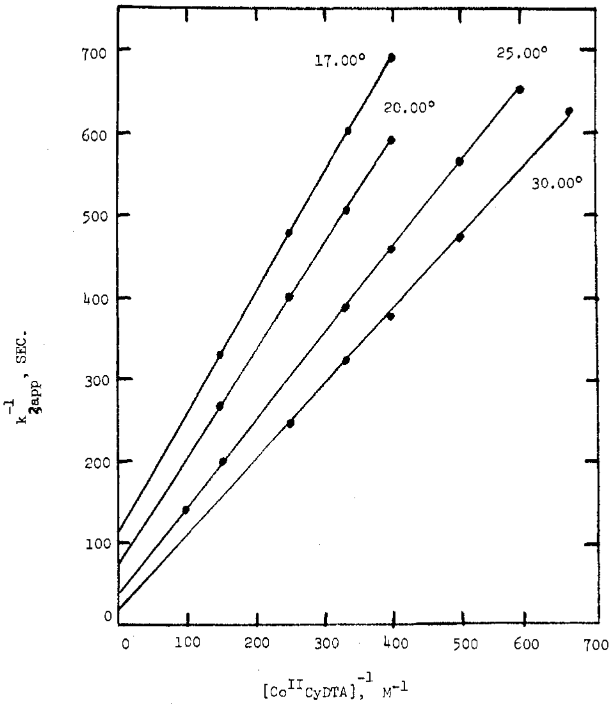

Figure 3. Double-reciprocal plot for the decomposition of I_1 to products for the Co^{II}CyDTA system.

A secondary reaction, corresponding to the oxidation of I_1 to I_2 (eq 2) found for the EDTA reaction,[11] was also found to occur in the present system. In order to check the possibility that k_{obsd} may contain a contribution due to the consumption of ferricyanide in the secondary reaction, additional experiments were conducted in which various concentrations of $Fe(CN)_6{}^{4-}$ were added to suppress the formation of I_2 (the Co^{III}-Fe^{III} binuclear intermediate). Results of these experiments are also listed in Table IV. Examination of the calculated values of k_1 in the last column of Table IV reveals a tendency to decrease slightly in most cases, as the ratio of [Co^{II}CyDTA] to [$Fe(CN)_6{}^{3-}$] increases, up to a point. Thereafter, the numbers fluctuate about a mean value in a random fashion. It is also clear that the addition of ferrocyanide ion does not alter the observed value of k_1 from this mean with any statistical significance except in the measurements at 8°. In the latter case, the ferrocyanide appears to cause k_1 to become smaller until a concentration of 5 × 10^{-3} M is reached. At each of the four temperatures the decision is made that k_1 becomes statistically invariant by means of the t test for the difference of two means, at the 95% significance level. Thus, in Table IV the last three sets of experiments are accepted at 25°, the last five at 18°, the last four at 13°, and the last three at 8°. The mean values for the accepted group, along with the overall standard error of the mean, are tabulated in Table V. A least-squares fit of the rate data to the Eyring equation gives the activation parameters $\Delta H_1{}^*$ = 1.9 ± 0.2 kcal/mol and ΔS^* = −35 ± 1 cal/deg mol.

Discussion

Two separate sources of evidence led Adamson and Gonick[7] to conclude that the successor complex, (EDTA)-Co^{III}-NC-$Fe^{II}(CN)_5{}^{5-}$, is the observed intermediate in the reaction between Co^{II}EDTA and $Fe(CN)_6{}^{3-}$. The first was that the paramagnetism of both the reactants disappears as soon as the two components are mixed, and the intermediate, like both Co^{III}EDTA and $Fe(CN)_6{}^{4-}$, is diamagnetic. The second was the absorption spectrum of the intermediate

Table IV. Kinetics of Formation of I_1 from $Co^{II}CyDTA + Fe(CN)_6{}^{3-}$ [a]

Temp, °C	$10^3[Co^{II}CyDTA]$, M	$10^5[Fe(CN)_6{}^{3-}]$, M	$[Fe(CN)_6{}^{4-}]$, M	N[b]	$10^{-3}k_1$, M^{-1} sec^{-1}
24.80	5.00	50.0	0	4	4.01 ± 0.11
	10.0	50.0	0	4	3.93 ± 0.08
	15.0	50.0	0	4	3.60 ± 0.05
	5.00	5.00	0	4	2.80 ± 0.21
	15.0	5.00	0	3	3.49 ± 0.16
	15.0	50.0	5×10^{-3}	6	3.58 ± 0.03
	15.0	50.0	2×10^{-2}	7	3.61 ± 0.04
18.25	5.00	50.0	0	4	3.03 ± 0.14
	10.0	50.0	0	4	2.89 ± 0.16
	15.0	50.0	0	4	3.25 ± 0.04
	5.00	5.00	0	4	3.28 ± 0.11
	15.0	5.00	0	4	2.89 ± 0.19
	15.0	50.0	5×10^{-3}	4	3.24 ± 0.03
	15.0	50.0	2×10^{-2}	6	3.24 ± 0.05
12.80	5.00	50.0	0	4	3.27 ± 0.01
	10.0	50.0	0	4	3.22 ± 0.02
	15.0	50.0	0	4	3.06 ± 0.01
	15.0	5.00	0	4	3.20 ± 0.18
	15.0	50.0	5×10^{-3}	8	2.92 ± 0.05
	15.0	50.0	2×10^{-2}	6	3.18 ± 0.03
8.00	5.00	50.0	0	4	2.88 ± 0.04
	10.0	50.0	0	4	2.97 ± 0.01
	15.0	50.0	0	4	3.02 ± 0.03
	5.00	5.00	0	7	3.24 ± 0.08
	15.0	5.00	0	3	2.98 ± 0.03
	15.0	50.0	5×10^{-4}	4	2.89 ± 0.02
	15.0	50.0	1×10^{-3}	4	2.84 ± 0.02
	15.0	50.0	2×10^{-3}	4	2.82 ± 0.04
	15.0	50.0	5×10^{-3}	6	2.75 ± 0.02
	15.0	50.0	1×10^{-2}	4	2.76 ± 0.09
	15.0	50.0	2×10^{-2}	6	2.74 ± 0.02

[a] $\mu = 0.660$, pH 5.00. [b] N refers to the number of replicates.

Table V. Calculated Rate Data for the Formation of I_1 from $Co^{II}CyDTA$ and $Fe(CN)_6{}^{3-}$

Temp, °C	$10^{-3}k_1$, M^{-1} sec^{-1}	Temp, °C	$10^{-3}k_1$, M^{-1} sec^{-1}
24.80 ± 0.01	3.58 ± 0.03	12.80 ± 0.01	3.03 ± 0.04
18.25 ± 0.01	3.20 ± 0.01	8.00 ± 0.01	2.75 ± 0.03

which is similar to the sum of the spectra of $Co^{III}EDTA$ and $Fe(CN)_6{}^{4-}$. This type of relationship between the spectrum of a binuclear complex and those of its component chromophores had been observed previously.[6,12] In the previous temperature-jump measurements with this system,[11] only one relaxation time was observed. Thus, no trace of the precursor complex is observed in this reaction.

In the present work, the spectral evidence supports the conclusion that in the reaction of the two Co^{II} complexes with $Fe(CN)_6{}^{3-}$, the intermediates are the cyano-bridged Co^{III}-Fe^{II} successor complexes. It must, therefore, be kept in mind, when considering rate constants and equilibrium constants for the fast reaction, that in the single observable step, both bond formation and electron transfer take place.

Weakliem and Hoard[13] have concluded from X-ray studies on $Co^{III}EDTA$ that the complex contains two nonequivalent types of acetate groups bonded to the cobalt. The two acetates rings which are coplanar with the nitrogen groups (in plane) are bent and strained while out-of-plane acetates are planar and strain free. The cobalt-oxygen bond length in the former case is 1.885 Å while in the latter case it is 1.915 Å. Terrill and Reilley[14] have discussed X-ray data which indicate that the same is true for $Co^{III}CyDTA$.

The cobalt(II) ion is somewhat larger than the cobalt(III) ion, which should therefore tend to reduce the amount of strain experienced by the in-plane acetate rings. A molecular model of the complex reveals, however, that most of this strain still exists in the $Co^{II}EDTA$ complex. The strained condition of the in-plane acetates should render them more susceptible to displacement by the incoming cyano group than the out-of-plane acetates.

Examination of the molecular models shows that when an acetate group is not complexed to the metal center in Co^{II}-EDTA, considerable freedom exists for rotation about the carbon–nitrogen and carbon–carbon bonds in the chelate molecule. As a result, the carboxylate oxygens are free to move away from the bridging cyano bonding site with little restriction. In contrast with this, the model for $Co^{II}CyDTA$ reveals that a displaced acetate is subject to considerable steric restriction in its movement. In particular, the methylene protons of the acetate group come into close proximity to the axial proton in the 3 position of the cyclohexane ring, as shown in Figure 4. Additional steric hindrance is encountered between the carboxyl group and the cyclohexane ring when rotation about the carbon–nitrogen bond is attempted. These interactions result in steric pressure to constrain the acetate to a position which is close to the cyano bridge bonding site.

The results reported here are in accord with the observations reported above. This steric restriction affects both the formation reaction and equilibria involving I_1 as well as its subsequent decomposition.

Formation of I_1. The observed fact that k_1 and K_1 for the $Co^{II}CyDTA$ are nearly $^1/_{20}$th as large as those for $Co^{II}EDTA$ reflects the reduced tendency for the CyDTA complex to form the binuclear species, and this is undoubtably related to the steric interference between the acetate group being displaced and the cyclohexane ring. The smaller value of K_1 for the CyDTA complex is corroborated by a larger acid dissociation constant for the $Co^{III}CyDTA \cdot H(H_2O)$ species

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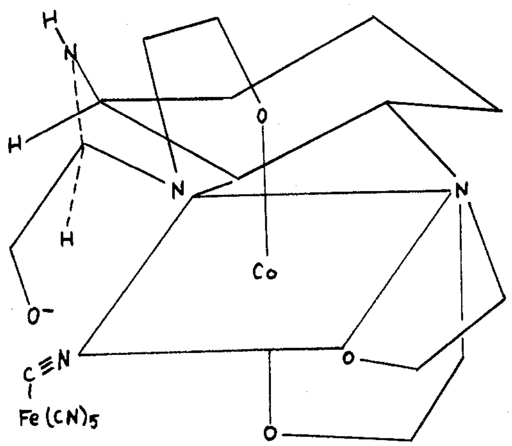

Figure 4. Steric hindrance in the (CyDTA)Co^{III}-NC-$Fe^{II}(CN)_5{}^{5-}$ intermediate.

(p$K_a \approx 1.0$), compared with the EDTA complex (p$K_a \approx 3.0$), which has been interpreted[15] as being similarly due to the steric restriction on the acetate group in the CyDTA complex. Also, Smith and Betts[16] have studied the formation of nitrito substitution on cobalt(III)-polyaminocarboxylic acid complexes and found that $Co^{III}(NO_2)$EDTA and $Co^{III}(NO_2)$-HEDTA form readily but that the corresponding complex of Co^{III}CyDTA does not form at all. This again appears to be due to the reluctance of the acetate group to move aside in favor of a NO_2^- group due to the presence of the cyclohexane ring.

It is possible, despite the absence of strain in the out-of-plane acetate rings, that the incoming cyano group in the present reaction displaces one of these acetate groups rather than an in-plane acetate. Terrill and Reilley[14] have examined the isotopic exchange of Co^{III}EDTA and Co^{III}CyDTA in acidic heavy water in an nmr study and found that only out-of-plane acetate protons exchange with deuterium. This exchange is believed to take place by protonation and enolization of the carbonyl group. It is probable that exchange occurs only on the out-of-plane acetate rings since they are planar. The bent configuration of the in-plane acetate rings prevents the formation of the enol π bond by skewing the π orbitals on the adjacent carbon atoms. Thus, if the formation of I_1 involves displacement of an out-of-plane acetate, then the steric hindrance would be even more severe due to the greater degree of interaction between acetate methylene protons and the axial protons in the 3 position of the cyclohexane ring.

Table VI. Comparison of Rates of Ring Closure for Co^{III}(chelate)·X Complexes at 25°

Complex	k_3, sec^{-1}	ΔH_3^*, kcal/mol	ΔS_3^*, cal/deg mol	Ref
Co^{III}EDTA·H_2O	1.7×10^{-3}	24.6	+11.3	22
Co^{III}EDTA·Cl	2.6×10^{-6}	22.8	−8.3	21
Co^{III}EDTA·$NCFe(CN)_5$	5.4×10^{-3}	25.4	+16.1	This work
Co^{III}CyDTA·H_2O	7.2×10^{-4}	18.8	−10.2	20
Co^{III}CyDTA·Cl	1.4×10^{-4}	21.9	−28	20
Co^{III}CyDTA·$NCFe(CN)_5$	2.2×10^{-2}	23.0	+10.9	This work

It is interesting to compare the experimental values of K_1 for the equilibria with ferricyanide ion with equilibrium constants reported in the literature for corresponding reactions with cyanide ion. Thus[17] $K_1 = 2000$ for the attack by CN^- on Co^{II}EDTA while $K_1 = 831$ in the present work for the attack by $Fe(CN)_6{}^{3-}$. Similarly[18] for the CN^- attack on Co^{II}CyDTA, $K_1 = 39$, while for $Fe(CN)_6{}^{3-}$ attack in the present study, $K_1 = 43.6$. Despite the obvious differences in ionic charge and the fact that no electron transfer accompanies cyanide addition, the equilibrium constants are remarkably similar. Such behavior is probably fortuitous. If the free energy requirement for reverse electron transfer is less than the free energy to bring about the chemical transformations to produce the activated state, then the similarity in the K_1 values noted above may be accounted for by the greater bond strength between cobalt and C-bonded cyanide compared with cobalt and N-bonded ferricyanide, which would tend to offset the lower electrostatic repulsion between reactants in the cyanide reaction. It may be noted that the standard enthalpies of reaction, $\Delta H_1°$, for the formation of the intermediates are very similar. This is to be expected since in each case the same processes take place; *i.e.*, the cyano bridge forms, displacing a bound acetate, and electron transfer occurs.

With a knowledge of the equilibrium constant and the forward rate constant, k_1, for each system, it is possible to calculate the magnitude of the reverse rate constant k_{-1}. When this calculation is carried out for the data at 25°, the values obtained for k_{-1} are approximately the same (82 sec^{-1} for Co^{II}CyDTA *vs.* 100 sec^{-1} for Co^{II}EDTA). One is tempted to conclude, since the reverse reaction is independent of the nature of the chelating ligand and the attendant steric effects, that this step occurs by a purely dissociative mechanism. However, since it is believed that the forward decomposition of I_1 to products is SN2 in nature, *vide infra*, and if the pendant acetate group assists in the expulsion of the bridging cyano group in that case, the same type of assistance could be expected for the reverse decomposition.

Spectrum of I_1. Use of the rigorous Rose-Drago method has permitted the accurate determination of the spectrum of the bridged intermediate I_1 for the Co^{II}CyDTA + $Fe(CN)_6{}^{3-}$ system, as shown in Figure 1. This spectrum may be compared with that for the corresponding EDTA intermediate as reported previously.[11] The two spectra are very similar in shape with λ_{max} 560 and ϵ_{max} 710 for the EDTA intermediate, and λ_{max} 540 and ϵ_{max} 685 for the CyDTA intermediate. The absorption spectra are similar in shape to the sum of the spectra for Co^{III}(chelate) and $Fe^{II}(CN)_6{}^{4-}$ in both cases, since the binuclear intermediates are composed of these chromophores.

Decomposition of I_1. In contrast with the formation data, the rate of decomposition of the intermediate in the Co^{II}-CyDTA system is 4 times faster than the corresponding Co^{II}-EDTA system. No electron transfer accompanies this step; only simple substitution of a chelate acetate group for the bridging cyano group is involved.

If I_1 decomposes by an SN2 mechanism in the present system it is expected that the EDTA complex would do so at a slower rate than the CyDTA complex since, although in both the displaced acetate must enter a strained position to force the bridging ligand out, in the CyDTA complex the entering acetate is held in a favorable position to do this as a result of the steric hindrance caused by the cyclohexane ring. This conclusion that bond making occurs before bond

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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; $Co^{II}\text{-}CyDTA^{2-}$, 28161-91-3; $[(CyDTA)Co^{III}\text{-}NC\text{-}Fe^{II}(CN)_6]^{5-}$, 38531-80-5.

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Contribution from the Department of Chemistry,
Seton Hall University, South Orange, New Jersey 07079

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

DANIEL H. HUCHITAL* and ROBERT J. HODGES

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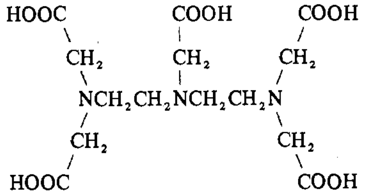
Diethylenetriaminepentaacetatocobaltate(II) [$Co^{II}DTPA$] is rapidly oxidized by ferricyanide ion to form a deep purple solution, and this color fades to a lighter solution. In this respect, the system is like the analogous $Co^{II}EDTA$- and Co^{II}-CyDTA-$Fe(CN)_6^{3-}$ systems. The rate of the slow 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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