Table II. Characteristic Infrared Bands in cm^{-1} [a]

Complex	ν(pyz)	ν(NO)		
		Nitrosyl	Nitro	Nitrito
$[(\mathrm{bipy})_2\mathrm{Ru(pyz)Cl}](\mathrm{PF}_6)$	1588 (s)			
$[(\mathrm{bipy})_2\mathrm{Ru(pyz)NO}_2](\mathrm{PF}_6)\cdot\mathrm{H}_2\mathrm{O}$	1585 (s)		1338 (s), 1294 (s)	1393 (sh), 1133 (s, br)
$[(\mathrm{bipy})_2\mathrm{ClRu(pyz)Ru(NO}_2)(\mathrm{bipy})_2](\mathrm{PF}_6)_2\cdot 2\mathrm{H}_2\mathrm{O}$			1340 (s), 1295 (2)	1395 (sh), 1135 (s, br)
$[(\mathrm{bipy})_2\mathrm{ClRu(pyz)Ru(NO)(bipy)}_2](\mathrm{PF}_6)_4$		1940 (vs)		
$[(\mathrm{bipy})_2\mathrm{ClRu(pyz)[Ru(bipy)}_2\mathrm{pyz]Ru(NO)(bipy)}_2](\mathrm{PF}_6)_6$		1942 (vs)		

[a] In KBr pellets; ±4 cm^{-1}. Abbreviations used are very strong (vs), strong (s), shoulder (sh), and broad (br).

dried over $\mathrm{P}_4\mathrm{O}_{10}$ *in vacuo* overnight, yield 60%. *Anal.* Calcd for $[(\mathrm{bipy})_2\mathrm{ClRu(pyz)[Ru(bipy)}_2\mathrm{pyz]}_n\mathrm{RuCl(bipy)}_2](\mathrm{PF}_6)_{2n+2}\cdot(n+2)\mathrm{H}_2\mathrm{O}$ ($n = 1$): C, 38.78; H, 2.94; N, 10.64; Cl, 3.37. Found: C, 38.38; H, 2.76; N, 10.80; Cl, 3.25. Calcd ($n = 2$): C, 38.01; H, 2.89; N, 10.59; Cl, 2.44. Found: C, 38.27; H, 3.09; N, 10.74; Cl, 2.30. Calcd ($n = 3$): C, 39.00; H, 2.87; N, 10.62. Found: C, 39.90; H, 3.02; N, 11.35. Calcd ($n = 4$): C, 37.25; H, 2.87; N, 10.55. Found: C, 38.01; H, 3.10; N, 10.06.

$[(\mathrm{bipy})_2\mathrm{ClRu(pyz)[Ru(bipy)}_2\mathrm{pyz]}_n\mathrm{Ru(NO)(bipy)}_2](\mathrm{PF}_6)_{2n+4}$. The nitrosyl complexes were prepared in methanol by adding acid to the corresponding nitrite complexes. As an example the preparation of $[(\mathrm{bipy})_2\mathrm{ClRu(pyz)Ru(NO)(bipy)}_2](\mathrm{PF}_6)_4$ is given below. $[(\mathrm{bipy})_2\mathrm{ClRu(pyz)Ru(NO}_2)(\mathrm{bipy})_2](\mathrm{PF}_6)_2$ (0.500 g, 0.391 mmol) was suspended with stirring in methanol (30 ml). To the suspension was added dropwise 6 ml of 70% HPF_6 and stirring was continued for several minutes. Ether was added and the deep red-brown precipitate was collected on a frit, reprecipitated three times from acetone–ether, washed twice with ether, air-dried, and finally dried over $\mathrm{P}_4\mathrm{O}_{10}$ *in vacuo* overnight, yield 90%. *Anal.* Calcd for $[(\mathrm{bipy})_2\mathrm{ClRu(pyz)Ru(NO)(bipy)}_2](\mathrm{PF}_6)_4$: C, 34.04; H, 2.32; N, 9.92; Cl, 2.29. Found: C, 33.86; H, 2.32; N, 9.83; Cl, 2.14. Calcd for $[(\mathrm{bipy})_2\mathrm{ClRu(pyz)[Ru(bipy)}_2\mathrm{pyz]Ru(NO)(bipy)}_2](\mathrm{PF}_6)_6$: C, 34.17; H, 2.59; N, 9.96; Cl, 1.49. Found: C, 35.10; H, 2.55; N, 9.97; Cl, 1.39. Elemental analyses were not obtained for the remainder of the nitrosyl and nitrite complexes since they were utilized as intermediates for the preparation of the longer chain polymeric complexes.

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Registry No. $[\mathrm{Ru(bipy)}_2(\mathrm{pyz})\mathrm{Cl}](\mathrm{PF}_6)$, 40537-43-7; $[\mathrm{Ru(bipy)}_2(\mathrm{pyz})\mathrm{NO}_2](\mathrm{PF}_6)\cdot\mathrm{H}_2\mathrm{O}$, 40548-18-3; $[\mathrm{Ru(bipy)}_2(\mathrm{BPE})\mathrm{Cl}](\mathrm{PF}_6)\cdot 2\mathrm{H}_2\mathrm{O}$, 40548-19-4; $[\mathrm{Ru(bipy)}_2(4,4'\text{-bipy})\mathrm{Cl}](\mathrm{PF}_6)\cdot\mathrm{H}_2\mathrm{O}$, 40548-20-7; $[\mathrm{Ru(bipy)}_2(\mathrm{pyz})_2](\mathrm{PF}_6)_2$, 40537-44-8; $[(\mathrm{bipy})_2\mathrm{ClRu(pyz)RuCl(bipy)}_2](\mathrm{PF}_6)_2\cdot 2\mathrm{H}_2\mathrm{O}$, 40548-21-8; $[(\mathrm{bipy})_2\mathrm{ClRu(BPE)RuCl(bipy)}_2](\mathrm{PF}_6)_2\cdot 2\mathrm{H}_2\mathrm{O}$, 40587-86-8; $[(\mathrm{bipy})_2\mathrm{ClRu}(4,4'\text{-bipy})\mathrm{RuCl(bipy)}_2](\mathrm{PF}_6)_2\cdot 2\mathrm{H}_2\mathrm{O}$, 40548-22-9; $[(\mathrm{bipy})_2\mathrm{ClRu(pyz)[Ru(bipy)}_2\mathrm{pyz]RuCl(bipy)}_2](\mathrm{PF}_6)_4\cdot\mathrm{H}_2\mathrm{O}$, 40548-23-0; $[(\mathrm{bipy})_2\mathrm{ClRu(pyz)[Ru(bipy)}_2\mathrm{pyz]}_2\mathrm{RuCl(bipy)}_2](\mathrm{PF}_6)_6\cdot 2\mathrm{H}_2\mathrm{O}$, 39296-34-9; $[(\mathrm{bipy})_2\mathrm{ClRu(pyz)[Ru(bipy)}_2\mathrm{pyz]}_3\mathrm{RuCl(bipy)}_2](\mathrm{PF}_6)_8\cdot 3\mathrm{H}_2\mathrm{O}$, 40548-24-1; $[(\mathrm{bipy})_2\mathrm{ClRu(pyz)[Ru(bipy)}_2\mathrm{pyz]}_4\mathrm{RuCl(bipy)}_2](\mathrm{PF}_6)_{10}\cdot 4\mathrm{H}_2\mathrm{O}$, 39296-35-0; $[(\mathrm{bipy})_2\mathrm{ClRu(pyz)Ru(NO)(bipy)}_2](\mathrm{PF}_6)_4$, 40537-45-9; $[(\mathrm{bipy})_2\mathrm{ClRu(pyz)[Ru(bipy)}_2\mathrm{pyz]Ru(NO)(bipy)}_2](\mathrm{PF}_6)_6$, 40537-46-0; $[(\mathrm{bipy})_2\mathrm{ClRu(pyz)Ru(NO}_2)(\mathrm{bipy})_2](\mathrm{PF}_6)_2\cdot 2\mathrm{H}_2\mathrm{O}$, 40537-47-1; $[\mathrm{Ru(bipy)}_2(\mathrm{NO})\mathrm{Cl}](\mathrm{PF}_6)_2$, 29102-12-3; $[\mathrm{Ru(bipy)}_2(\mathrm{NO})(\mathrm{NO}_2)](\mathrm{PF}_6)_2$, 29240-99-1; $\mathrm{Ru(bipy)}_2\mathrm{Cl}_2$, 15746-57-3.

Contribution from the Department of Chemistry,
Western Washington State College, Bellingham, Washington 98225

Oxalate Anation of α-*cis*-Ethylenediamine-*N*,*N*′-diacetatodiaquocobalt(III) Ion in Slightly Acidic Aqueous Medium[1]

JOHN A. WEYH,* ARVID K. NEWLUN, TIMOTHY J. BAKER and TOD K. SHIOYAMA

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The reaction of α-*cis*-$\mathrm{Co(EDDA)(OH_2)_2}^+$ with members of the oxalate system in the pH range 4.5–5.2 yields geometrically pure β-*cis*-$\mathrm{Co(EDDA)(C_2O_4)}^-$. Evidence indicates that the geometry change occurs at or after the rate-determining step. The reaction appears to proceed *via* ion-pair equilibration followed by rate-determining substitution. Values for the association constants for the ion pairs α-*cis*-$\mathrm{Co(EDDA)(OH_2)_2}^+,\mathrm{HC_2O_4}^-$ and α-*cis*-$\mathrm{Co(EDDA)(OH_2)_2}^+,\mathrm{C_2O_4}^{2-}$ are 41 and 72, respectively, at 38° and $\mu = 0.50$. In the pH range studied, the species $\mathrm{Co(EDDA)(OH)(OH_2)}^0$ makes an important contribution to the generation of product.

Introduction

Harris and coworkers have recently reported on their studies of the anation of various aquo-containing cobalt(III) and chromium(III) complexes with members of the oxalate system.[2-4] Effectively they proposed an ion-pair equilibration between complex and the oxalate member prior to the slower rate-determining ligand–water dissociation. Other workers[5] have proposed similar mechanisms for numbers of anation reactions involving coordination complexes.

We have chosen to investigate the oxalate anation of α-*cis*-ethylenediamine-*N*,*N*′-diacetatodiaquocobalt(III) ion (α-*cis*-$\mathrm{Co(EDDA)(OH_2)_2}^+$) for numbers of reasons.[6]

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[1] Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 8–13, 1973.

[2] P. M. Brown and G. M. Harris, *Inorg. Chem.*, 7, 1872 (1968).

[3] S. C. Chan and G. M. Harris, *Inorg. Chem.*, **10**, 1317 (1971).

[4] H. Kelm and G. M. Harris, *Inorg. Chem.*, 6, 706 (1967).

[5] (a) S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, **21**, 1745 (1968); (b) R. E. Hamm, R. L. Johnson, R. H. Perkins, and R. E. Davis, *J. Amer. Chem. Soc.*, **80**, 4469 (1958).

First of all we wanted to see if the generally emerging pattern of anation, *i.e.*, ion-pair equilibration followed by rate-determining substitution, applies to our system.

Second, the values for the ion-pair association constants (obtained from kinetic studies in aqueous solution) reported in the literature overwhelmingly are for highly charged complexes reacting with highly charged ligands of the opposite sign. With regard to opposites in sign the 3+,1− and 2+, 2− complex-ligand charge magnitude appears to be the smallest reported. There has, however, recently appeared the value for an ion association constant involving a 3+,0 interaction.[2] Further, ion association constant values have appeared for species of the same charge sign.[4] In this picture there is a complete lack of data relating to the interaction of complex and ligand where the magnitude of charges is smaller than above. Specifically we refer to the interactions of a 1+ charged complex with 1− and 2− charged ligands. Since α-*cis*-$Co(EDDA)(OH_2)_2^+$ is singly charged and, depending on pH, $HC_2O_4^-$ and $C_2O_4^{2-}$ can be present in solution, this appears to be a likely choice of system for study.

Finally, in the pH region studied, the reaction of α-*cis*-$Co(EDDA)(OH_2)_2^+$ with oxalate occurs with a 100% effective change in geometry. The product of the reaction is pure β-*cis*-$Co(EDDA)(C_2O_4)^-$. We wanted to learn as much as possible regarding the geometry change relative to the anation reaction.

Experimental Section

Ethylenediamine-*N,N'*-diacetic acid was used as received from Pfaltz and Bauer, Inc. All other chemicals were reagent quality. Distilled water was used throughout.

α-*cis*-$[Co(EDDA)(OH_2)_2]ClO_4$ was prepared by the method of Kuroda and Watanabe.[7] Elemental analysis was performed by Galbraith Laboratories, Inc. *Anal.* Calcd for α-*cis*-$[Co(EDDA)(OH_2)_2]ClO_4$ ($CoC_6H_{14}O_{10}N_2Cl$): C, 19.55; H, 3.83; N, 7.60. Found: C, 19.41; H, 3.77; N, 7.59. Aqueous solutions of this compound gave molar absorptivities and peak positions as previously reported.[7]

The method employed in the determination of the first dissociation constant of α-*cis*-$Co(EDDA)(OH_2)_2^+$ was similar to that outlined by Bjerrum and Rasmussen.[8] A 0.0231-g sample (6.25×10^{-5} mol) of the complex was dissolved in 25.00 ml of H_2O and $NaNO_3$ was added so as to have $\mu = 0.50$ at 50% of neutralization. The sample was then titrated with standardized, carbonate-free NaOH. The pH meter was calibrated using conventional buffer solutions and a strong acid buffer made from a standardized nitric acid solution. All solutions were adjusted to the appropriate ionic strength with $NaNO_3$.

All kinetic runs were made on a Coleman Perkin-Elmer Model 46 spectrophotometer which was fitted with a constant-temperature cell block in which matched 1-cm cells were used. A constant-temperature water bath and pump were utilized in circulating thermostated water through the block surrounding the sample and reference cells. The temperature within the block was maintained within ±0.05° of the desired value.

Rate constants for the anation of α-*cis*-$Co(EDDA)(OH_2)_2^+$ with oxalate were determined spectrophotometrically at 385 nm. This corresponds closely to a peak position for both reactant and product with the molar absorptivities being 76[7] and 205,[9] respectively. "Infinite" absorbance measurements were made 12–24 hr after the reaction was begun depending upon hydrogen ion and temperature conditions. These readings were checked intermittently for constancy. The complex concentration was fixed at 2.50×10^{-3} *M* in all of the experiments reported.

The procedure for a typical kinetic run is outlined as follows. Amounts of sodium oxalate and oxalic acid were weighed out such that pseudo-first-order kinetics was obtained at the desired acidity. These were then dissolved in 25.00 ml of H_2O, followed by the addition of the necessary amount of $NaNO_3$. The flask was then stoppered and placed in the water bath for temperature equilibration. The reaction was initiated by adding solid complex to the solution with rapid stirring. Three milliliters of the solution was transferred to the dry, equilibrated 1-cm cell, and the change in absorbance followed as a function of time. The reference cell contained H_2O. All solutions and equipment were allowed at least 30 min to attain temperature equilibrium.

Results and Discussion

In aqueous solutions with neutral to slightly acidic pH, anation of α-*cis*-$Co(EDDA)(OH_2)_2^+$ ion with $HC_2O_4^-$ and $C_2O_4^{2-}$ results in the formation of geometrically pure β-*cis*-$Co(EDDA)(C_2O_4)^-$. The visible spectrum of the product (both peak positions and molar absorptivities) agrees within experimental error with that reported by Kuroda and Watanabe.[9] Further, anion-exchange chromatography of the reaction mixture, after approximately 10 half-lives, yields no positive- or zero-charged complexes and only one anionic species with 1− charge characteristics. No trace of the α-*cis*-$Co(EDDA)(C_2O_4)^-$ isomer could be found on the column.

No spectral evidence appeared during any of the experiments which would indicate the presence of an intermediate in the anation reaction. Further substantiation of this contention is the fact that determination of k_{obsd} at 525 nm gave, within 1%, the results obtained at 385 nm.[10] Hence, spectrophotometrically speaking, the reaction could be depicted simply as

$$\alpha\text{-}cis\text{-}Co(EDDA)(OH_2)_2^+ + \left\{\begin{matrix} HC_2O_4^- \\ C_2O_4^{2-} \end{matrix}\right\} \rightarrow \beta\text{-}cis\text{-}Co(EDDA)(C_2O_4)^-$$

A series of kinetic runs was made systematically varying $[H^+]$, C_{ox} (total oxalate concentration), temperature, and ionic strength. C_{ox} was large enough to ensure the observation of pseudo-first-order kinetics. In all cases plots of $-\log (A_\infty - A_t)$ *vs.* *t* were linear for several half-lives. The slope of each line allowed the determination of k_{obsd} for each condition since slope $= k_{obsd}/2.303$.

Table I lists the various values of k_{obsd} obtained as a function of total oxalate concentration, hydrogen ion concentration, and temperature. Duplicate runs generally gave k_{obsd} values that agreed within 2% of the original. The effect of ionic strength on k_{obsd} at 50.50°, pH 4.9, and $C_{ox} = 7.50 \times 10^{-2}$ *M* is as follows: $\mu = 0.50$, $10^4k_{obsd} = 8.14$ sec^{-1}; $\mu = 1.00$, $10^4k_{obsd} = 6.75$ sec^{-1}; $\mu = 1.50$, $10^4k_{obsd} = 5.39$ sec^{-1}.

Hydrogen ion concentration affects k_{obsd} in an inverse, almost direct fashion. The $[H^+]$ is held constant by the $HC_2O_4^-$-$C_2O_4^{2-}$ buffer system. Further, it is noted that as C_{ox} increases, k_{obsd} increases but not nearly in direct proportion. In fact, it appears that k_{obsd} is approaching a limiting value as C_{ox} continues to increase. Such behavior could be interpreted as being indicative of ligand oxalate-reactant complex ion-pair equilibration prior to the rate-determining step.

As indicated by the limiting nature of k_{obsd} *vs.* C_{ox}, a plot of k_{obsd}^{-1} *vs.* C_{ox}^{-1} is linear at all hydrogen ion concentrations and temperatures studied. Such a plot at 50.50° is given in Figure 1.

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(6) The terms trans, α-cis, and β-cis which describe the possible geometries of EDDA in an octahedral environment are defined by P. J. Garnett, D. W. Watts, and J. I. Legg, *Inorg. Chem.*, **8**, 2534 (1969).

(7) K. Kuroda and K. Watanabe, *Bull. Chem. Soc. Jap.*, **44**, 1034 (1971).

(8) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

(9) K. Kuroda and K. Watanabe, *Bull. Chem. Soc. Jap.*, **44**, 2550 (1971).

(10) Comparing the analogous *cis*-$Co(en)_2(OH_2)_2{}^{3+}$-oxalate system[3] with the system under study one might expect to find the intermediate $Co(EDDA)(OH)(C_2O_4)^{2-}$ in the present study. Considering, however, the charge of the analogous $Co(en)_2(OH)(C_2O_4)^0$ intermediate with $Co(EDDA)(OH)(C_2O_4)^{2-}$ and remembering that the present study was carried out at pH ~5 as compared to above pH 7 for the en system, it is not surprising that no intermediate is observed.

Scheme I

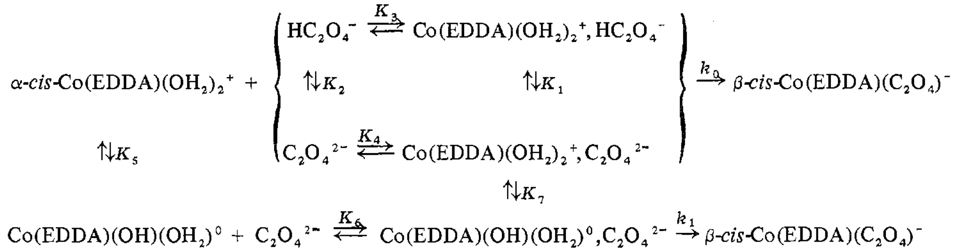

Table I. Pdeudo-First-Order Rate Constants for Reaction of α-*cis*-Co(EDDA)(OH$_2$)$_2^+$ with Oxalate ($\mu = 0.5$): $10^4 k_{\text{obsd}}$, sec^{-1} (C_{ox}, M)

	$10^5[\text{H}^+], M$	
3.1	1.2	0.62
	(a) 38.00°	
0.246 (0.0360)	0.652 (0.0300)	1.45 (0.0418)
0.253 (0.0390)	0.801 (0.0750)	1.55 (0.0550)
0.271 (0.0480)	0.860 (0.120)	1.60 (0.0825)
0.290 (0.0570)	0.871 (0.180)	1.68 (0.110)
0.305 (0.0690)		1.72 (0.165)
0.329 (0.105)		
0.336 (0.127)		
0.336 (0.150)		
	(b) 44.50°	
1.01 (0.0375)	1.61 (0.0150)	3.75 (0.0275)
1.20 (0.0750)	2.19 (0.0300)	4.65 (0.0550)
1.27 (0.113)	2.78 (0.0600)	4.99 (0.0825)
1.31 (0.150)	2.88 (0.0900)	5.49 (0.110)
	2.99 (0.120)	5.54 (0.165)
	3.10 (0.180)	
	(c) 50.50°	
2.56 (0.0480)	7.14 (0.0480)	11.9 (0.0330)
2.90 (0.0690)	8.14 (0.0750)	13.5 (0.0418)
3.29 (0.105)	8.98 (0.120)	14.5 (0.0550)
3.41 (0.128)	9.60 (0.180)	16.0 (0.0825)
		16.6 (0.110)

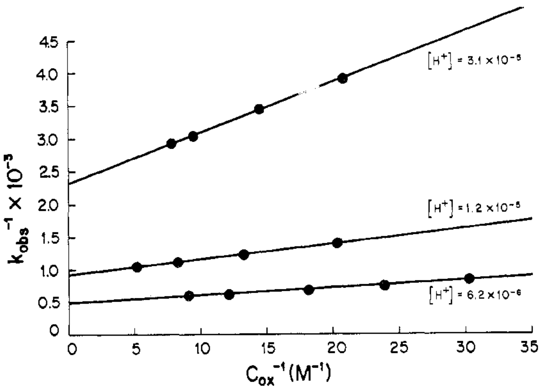

Figure 1. A plot of k_{obsd}^{-1} *vs.* C_{ox}^{-1} at 50.50° and $\mu = 0.500$ in the oxalate anation of α-*cis*-Co(EDDA)(OH$_2$)$_2^+$.

A mechanism which is in agreement with the experimental data for the HC$_2$O$_4^-$-C$_2$O$_4^{2-}$ anation of α-*cis*-Co(EDDA)(OH$_2$)$_2^+$ is shown in Scheme I.

By appropriate substitution[11] the proposed mechanism yields the rate law

$$\frac{d[P]}{dt} = \frac{(k_0[\text{H}^+]^2K_3 + k_0[\text{H}^+]K_2K_4 + k_1K_2K_5K_6)C_{\text{ox}}}{([\text{H}^+] + K_5)([\text{H}^+] + K_2) + ([\text{H}^+]^2K_3 + [\text{H}^+]K_2K_4 + K_2K_5K_6)C_{\text{ox}}}(C_{\text{Co}} - P) \qquad (1)$$

where P = β-*cis*-Co(EDDA)(C$_2$O$_4$)$^-$; $C_{\text{ox}} = [\text{HC}_2\text{O}_4^-] + [\text{C}_2\text{O}_4^{2-}]$; $C_{\text{Co}} - P$ = concentration of all cobalt-containing complexes which have not yet passed through the rate-determining step. From the rate law it is clear that

$$1/k_{\text{obsd}} = \frac{[\text{H}^+]^2K_3 + [\text{H}^+]K_2K_4 + K_2K_5K_6}{k_0([\text{H}^+]^2K_3 + [\text{H}^+]K_2K_4) + k_1K_2K_5K_6} + \frac{[\text{H}^+]^2 + (K_2 + K_5)[\text{H}^+] + K_2K_5}{k_0([\text{H}^+]^2K_3 + [\text{H}^+]K_2K_4) + k_1K_2K_5K_6}\left(\frac{1}{C_{\text{ox}}}\right) \qquad (2)$$

Hence a plot of k_{obsd}^{-1} *vs.* C_{ox}^{-1} should be linear.

Perhaps a less prejudiced initial proposal of the mechanism might indicate the passage of Co(EDDA)(OH$_2$)$_2^+$,HC$_2$O$_4^-$ and Co(EDDA)(OH$_2$)$_2^+$,C$_2$O$_4^{2-}$ to product *via* the distinct rate constants k_0 and k_0', respectively. Such a change would require, in eq 1, the replacement of k_0 in the numerator term $k_0[\text{H}^+]K_2K_4$ with k_0'. This more objective mechanism was not proposed initially for the following reasons. First, one might expect near equality for k_0 and k_0' since, in both cases, members of the oxalate system are loosely bound by electrostatic attraction in the outer coordination sphere of Co(III). Indeed, ligand-water substitution of a dissociative nature would even enhance this view. Second, because of experimental evidence, Brown and Harris[2] have proposed a similar type of rate constant equality in the oxalate anation of *cis*-Co(en)$_2$(OH$_2$)$_2^{3+}$. Finally, mathematical analysis of our experimental data indicated an inability to distinguish between k_0 and k_0'. Hence in our proposed mechanism we indicate $k_0' = k_0$.

In the proposed mechanism it is not possible to exclude either the Co(EDDA)(OH)(OH$_2$) pathway or the pathways involving α-*cis*-Co(EDDA)(OH$_2$)$_2^+$ as the initial reactant. If any pathway is excluded, the mechanism then predicts a constant intercept with no [H$^+$] dependence.[12] Since the intercept and the slope for the above inverse plot vary almost directly with [H$^+$], we must conclude that all pathways are important and further that each pathway produces β-*cis*-Co(EDDA)(C$_2$O$_4$)$^-$.[13]

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[11] Because of the circular nature of the various equilibria $K_1K_3 = K_2K_4$ and $K_4K_7 = K_5K_6$.

[12] If the pathway involving Co(EDDA)(OH)(OH$_2$)^0 is excluded the intercept term in eq 2 becomes

$$\frac{[\text{H}^+]K_3 + K_2K_4}{k_0([\text{H}^+]K_3 + K_2K_4)} = \frac{1}{k_0}$$

Similarly, if the pathway involving α-*cis* Co(EDDA)(OH$_2$)$_2^+$ is excluded, the intercept term becomes $K_2K_5K_6/k_1K_2K_5K_6 = 1/k_1$.

[13] Since $K_2 >> K_5$ and $K_2K_5 << [\text{H}^+]^2$ and $[\text{H}^+]K_2$ (see Table III), the slope in eq 2 reduces to

$$S = [\text{H}^+]\frac{[\text{H}^+] + K_2}{k_0([\text{H}^+]^2K_3 + [\text{H}^+]K_2K_4) + k_1K_2K_5K_6}$$

Similarly the intercept reduces to

$$I = [\text{H}^+]\frac{[\text{H}^+]K_3 + K_2K_4}{k_0([\text{H}^+]^2K_3 + [\text{H}^+]K_2K_4) + k_1K_2K_5K_6}$$

Hence nearly direct dependence of slope and intercept on [H$^+$] is expected.

There are nine rate and equilibrium constants defined in the proposed mechanism. K_2 has been previously measured. After evaluation of various reported values, we used $K_2 = 6.2 \times 10^{-5}$ with negligible temperature dependence in the region studied. Our experimental determination of K_5 yielded a value of $(4.6 \pm 0.1) \times 10^{-8}$. Hence α-*cis*-Co(EDDA)(OH_2)$_2^+$ is a much weaker acid than *cis*-Co(en)$_2$(OH_2)$_2^{3+}$ [8] as would be expected simply on the basis of charge differences. The values for K_1 and K_7 are obtained from the circular nature of the various equilibria. Referring to the expression for the intercept in eq 2, since K_3, K_4, and K_6 are expected to be of the same order of magnitude and since $[H^+]^2$ and $[H^+]K_2 >> K_2K_5$, one will only be able to extract from the data a composite value of k_1K_6. Hence direct extraction of k_0, K_3, K_4, and k_1K_6 from the data is indicated.

A program was written which allowed, using an iterative technique, the extraction of the best-fit values of k_0, K_3, K_4, and k_1K_6 based on the experimentally obtained slopes and intercepts from the various k_{obsd}^{-1} *vs.* C_{ox}^{-1} plots. The above-mentioned values of K_2 and K_5 were also used in the calculation. Table II shows the results of the theoretical fit of the experimental slopes and intercepts. Table III indicates the values obtained for the individual constants describing the α-*cis*-Co(EDDA)(OH_2)$_2^+$-oxalate system.

Since K_6 cannot be determined individually, values of K_7 cannot be obtained. A reasonable expectation for K_6 might be in the range 1-100. Using this range one notes that $k_1 >> k_0$. This is quite reasonable and has been noted in other Co(III) systems.[3,5a,14] It is felt that the OH^- group in the inner coordination sphere of the Co(III) complex labilizes the remaining H_2O with respect to substitution. Hence the k_1 pathway for the generation of product appears very favorable as compared to k_0. However because of the small value of K_5 and the pH conditions used in this study, all pathways are equally important.

K_1 is slightly larger than K_2 and lacks temperature dependence in the range studied. Similar behavior has been noted in other Co(III) systems.[2,15]

Table IV lists various Co(III) and Cr(III) ion pairs and their respective ion association constants. It is noted that our values for the 1+,1− and 1+,2− interactions complement the table quite well. The data indicate a general increase in K_{IP} as charge differences between complex and prospective ligand increase. This would be expected on a purely electrostatic basis. The two systems involving 2+,2− interactions do not seem to follow this trend. Perhaps this is partly attributable to the presence of a hydroxyl group in the coordination sphere of Co(III) in each. However, enough data has not been accumulated on these systems to make any definite statement.

The temperature variation in k_0 was utilized to calculate its activation parameters using the absolute reaction rate theory of Eyring.[16] For k_0, $\Delta H^\ddagger = 27.6 \pm 1.3$ kcal mol^{-1} and $\Delta S^\ddagger = +1.6 \pm 1.1$ eu.

Table II. Theoretical Fit of Experimental Slopes and Intercepts

Slope	Exptl	Calcd	Intercept	Exptl	Calcd
		38.00°			
1[a]	4.60×10^2	4.15×10^2	1	2.67×10^4	2.56×10^4
2[a]	1.57×10^2	1.65×10^2	2	1.05×10^4	1.10×10^4
3[a]	7.6×10^1	8.2×10^1	3	5.25×10^3	5.64×10^3
		44.50°			
1	1.24×10^2	1.32×10^2	1	6.80×10^3	7.30×10^3
2	4.73×10^1	4.97×10^1	2	2.95×10^3	2.99×10^3
3	2.61×10^1	2.42×10^1	3	1.63×10^3	1.50×10^3
		50.50°			
1	7.68×10^1	7.01×10^1	1	2.32×10^3	2.43×10^3
2	2.32×10^1	2.51×10^1	2	9.30×10^2	9.62×10^2
3	1.1×10^1	1.20×10^1	3	4.95×10^2	4.79×10^2

[a] At slope 1, $[H^+] = 3.1 \times 10^{-5}$ *M*; slope 2, $[H^+] = 1.2 \times 10^{-5}$ *M*; slope 3, $[H^+] = 0.62 \times 10^{-5}$ *M*. This pattern is followed for all slopes and intercepts.

Table III. Values of Parameters Describing the α-*cis*-Co(EDDA)(OH_2)$_2^+$–Oxalate System[a]

Temp, °C	10^5k_0, sec^{-1}	K_3	K_4	10^4K_1	k_1K_6	K_7
38.00	1.2	41	72	1.1	1.67	. . .
44.50	3.2	36	65	1.1	5.80	. . .
50.50	7.0	20	42	1.1	11.8	. . .

[a] Uncertainties in the parameters reported here are related to the relative differences between the calculated and the experimental slopes and intercepts as well as the experimental error involved in their determination. Using these guidelines we report the relative uncertainties for the listed kinetic parameters to be ±6–10%.

Table IV. Ion Association Constants for Various Co(III) and Cr(III) Systems

Ion pair	K_{IP} (temp, °C)	Ref
cis-Cr(C_2O_4)$_2$(OH_2)$_2^-$,$C_2O_4^{2-}$	1.9 (50)	*a*
cis-Cr(C_2O_4)$_2$(OH_2)$_2^-$,$HC_2O_4^-$	0.85 (50)	*a*
cis-Co(en)$_2$(OH_2)$_2^{3+}$,$H_2C_2O_4$	13 (40)	*b*
α-*cis*-Co(EDDA)(OH_2)$_2^+$,$HC_2O_4^-$	41 (38)	*c*
α-*cis*-Co(EDDA)(OH_2)$_2^+$,$C_2O_4^{2-}$	72 (38)	*c*
trans-Co(en)$_2$(OH)(OH_2)$^{2+}$,HPO_4^{2-}	60 (48)	*d*
Co(en)$_2$(OH)(OH_2)$^{2+}$,$C_2O_4^{2-}$	6 (25)	*e*
cis-Co(en)$_2$(OH_2)$_2^{3+}$,$HC_2O_4^-$	119 (40)	*b*
Co(NH_3)$_6^{3+}$,$C_2O_4^{2-}$	200 (25)	*f*

[a] See ref 4. [b] See ref 2. [c] This work. [d] See ref 5a. [e] See ref 3. [f] T. P. Jones, W. E. Harris, and W. J. Wallace, *Can. J. Chem.*, 39, 2371 (1961).

It would be very useful to have available the results of a water-exchange study on the α-*cis*-Co(EDDA)(OH_2)$_2^+$ system. This would allow comparison of exchange and anation results and perhaps allow a suggestion as to the mechanistic nature of the slow step in the anation reaction. Lacking this information it still is possible to compare data for the slow step in the anation of α-*cis*-Co(EDDA)(OH_2)$_2^+$ with exchange and anation data in the *cis*-Co(en)$_2$(OH_2)$_2^{3+}$ system. Kruse and Taube[14] have suggested that the data for water exchange in the *cis*-Co(en)$_2$(OH_2)$_2^{3+}$ system are more compatible with a dissociative activation process. Comparing the data for the oxalate anation of *cis*-Co(en)$_2$(OH_2)$_2^{3+}$ with the water-exchange data, Brown and Harris[2] have suggested that the slow step in the anation reaction involves the dissociation of a ligand-water molecule in the *cis*-Co(en)$_2$(OH_2)$_2^{3+}$, ox ion pair. For *cis*-Co(en)$_2$(OH_2)$_2^{3+}$ the activation parameters for k_{ex} are $\Delta H^\ddagger = 28.8$ kcal, $\Delta S^\ddagger = +15$ eu; for k_0 (k_0 has the same meaning as in our system) $\Delta H^\ddagger = 24.8$ kcal, $\Delta S^\ddagger = +1.5$ eu. For k_0 in the α-*cis*-Co(EDDA)(OH_2)$_2^+$ system $\Delta H^\ddagger = 27.6$ kcal and $\Delta S^\ddagger = +1.6$ eu. The rate constants at a given temperature for both systems are similar with k_{ex} being somewhat larger than k_0 in the *cis*-Co(en)$_2$(OH_2)$_2^{3+}$ system. Hence it is seen that the data suggest that the k_0 steps in the oxalate anation reactions involving both α-*cis*-Co(EDDA)(OH_2)$_2^+$ and *cis*-Co(en)$_2$(OH_2)$_2^{3+}$ may be similar. Without water-exchange data for the α-*cis*-Co(EDDA)(OH_2)$_2^+$ system this is all that can be stated.

With regard to the geometry change during the anation

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(16) H. Eyring, *Chem. Rev.*, 17, 65 (1935).

reaction it can be said that this change must occur at or after the slow rate-determining step. Spectral data indicate that the reaction does not occur *via* the process of isomerization followed by anation.

We are continuing our investigation of this system in both acidic and slightly basic media. In the pH range 7-9 we hope to obtain individual values for k_1 and K_6. Anation experiments conducted at pH 1 or below indicate that no geometry change occurs and that the product of the reaction is α-*cis*-Co(EDDA)(C_2O_4)$^-$.

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Registry No. α-*cis*[Co(EDDA)(OH_2)$_2$]ClO_4, 32715-40-5; $H_2C_2O_4$, 144-62-7; β-*cis*-Co(EDDA)(C_2O_4)$^-$, 26135-71-7.

Contribution from the Department of Chemistry,
Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

Stereochemistry of β-Diketone Complexes of Cobalt(III). XII. Kinetics and Mechanism of the Isomerization of Some *trans*-Anionopyridinebis(acetylacetonato)cobalt(III) Complexes

D. R. HERRINGTON and L. J. BOUCHER*

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Kinetic studies have been carried out in $CDCl_3$ on the trans–cis isomerization of [Co(acac)$_2$(X)(py)] where $X^- = N_3^-$, NO_2^-, CN^-, and NCO^-. Rate constants were determined over a temperature range of 29–60° by pmr methods, and activation and equilibrium parameters were obtained. At 29°, the first-order rate constants are $(1.92 \pm 0.13) \times 10^{-4}$ sec^{-1} for $X^- = N_3^-$, $(1.75 \pm 0.20) \times 10^{-5}$ sec^{-1} for $X^- = NCO^-$, and $(1.06 \pm 0.05) \times 10^{-6}$ sec^{-1} for $X^- = NO_2^-$. The enthalpies and entropies of activation, ΔH^* and ΔS^*, are as follows: 26.7 ± 2.7 kcal/mol and 13.1 ± 9.1 eu for $X^- = N_3^-$; 33.2 ± 2.9 kcal/mol and 29.8 ± 9.9 eu for $X = NCO^-$; 38.8 ± 1.0 kcal/mol and 42.9 ± 3.4 eu for $X^- = NO_2^-$. The corresponding complex where $X^- = CN^-$ does not isomerize in $CDCl_3$. The isomerization rate order is $N_3^- > NCO^- > NO_2^- > CN^-$. Several dissociative mechanisms involving a trigonal-bipyramidal intermediate are suggested. The trend in the rates may be attributed to the π-donor ability of X^- to stabilize the intermediate. The synthesis of *trans*-[Co(acac)$_2$(NCO)(py)] is described.

In previous work involving the synthesis and characterization of a number of new bis(acetylacetonato)cobalt(III) complexes,[1,2] marked differences were noted in the reactivity of the complexes in solution. Such changes appeared to be correlated with changes in the anions bound to the cobalt. For example, while *cis*-[Co(acac)$_2$(CN)$_2$]$^-$ is completely inert in aqueous solution, *cis*-[Co(acac)$_2$(N_3)$_2$]$^-$ rapidly undergoes a complex series of solvolyses and isomerizations under the same conditions. *cis*-[Co(acac)$_2$(NO_2)$_2$]$^-$ also undergoes isomerization and subsequent solvolysis in aqueous solution,[3] but at a much slower rate than the *cis*-diazide.

In an effort to determine the nature of the effect exerted by the anions on the reacitivity of the cobalt(III) acetylacetonates, a kinetic study of the trans → cis isomerization of [Co(acac)$_2$(X)(py)] in chloroform, where $X^- = N_3^-$, NCO^-, CN^-, and NO_2^-, was undertaken. The neutral complexes may be studied in a nonpolar, noncoordinating solvent which eliminates the possibility of solvolysis as well as ion-pair effects. The isomerization of the acetylacetonates is easily monitored by means of nmr spectroscopy.

Experimental Section

Materials. The trans isomers of [Co(acac)$_2$(N_3)(py)],[1] [Co(acac)$_2$(CN)(py)],[2] and [Co(acac)$_2$(NO_2)(py)][4] were prepared as previously described. The solvent used in the kinetic runs was chloroform-*d*, 99.8% purity, containing 1% TMS (Diaprep, Inc.).

Synthesis of *trans*-[Co(acac)$_2$(NCO)(py)]. Two grams of [Co(acac)$_2$] (0.0078 mol) was dissolved in 100 ml of water. After the addition of 1.25 g of potassium cyanate (0.0156 mol) and 2 ml of pyridine (0.0248 mol), 2 ml of 30% hydrogen peroxide solution (0.0176 mol) was added dropwise. The reaction mixture was stirred at 25° for 4 hr, at which point the crude product was filtered and air-dried. The green-brown product was dissolved in a minimum of chloroform and deposited on a 2.5-cm column packed to a height of 30 cm with 60–100 mesh Florisil (Floridin Co.). Elution with benzene–10% methanol resulted in the rapid movement of a single concentrated green band down the column. This component, the pure product, was collected and evaporated to dryness. The impurities in the reaction mixture remain on the top of the column. The product was recrystallized from chloroform–petroleum ether and air-dried. The yield was 0.23 g (8%). *Anal.*[5] Calcd for $C_{16}H_{19}N_2O_5Co$, [Co(acac)$_2$(NCO)(py)]: C, 50.79; H, 5.03; N, 7.41. Found: C, 50.49; H, 4.97; N, 7.22; mp 160°. The pmr spectrum of this compound in $CDCl_3$ exhibits methyl resonance at −2.22 ppm downfield from TMS and a single methine resonance at −5.38 ppm. The asymmetric stretch of the coordinated cyanate gives a single band at 2230 cm^{-1} in the ir spectrum.

Kinetic Measurements. The kinetic measurements of the trans → cis isomerization were made using a Varian HA-100 high-resolution 100-MHz nmr spectrometer equipped with a Varian Model V-4343 variable-temperature controller. The temperature of the probe prior to each run was determined (±0.1°) by measuring the methylene coupling constant of an ethylene glycol sample. Each complex was measured at five different temperatures with three runs being made at each temperature and averaged. In each case, 15 mg of complex was dissolved in 400 μl of deuteriochloroform, giving a 0.1 *M* solution. Spectra were recorded in the methyl region of the spectra at 50-Hz sweep width at various time intervals (Figure 1) until the sample reached equilibrium (~4 half-lives). For cases in which the time required for attainment of equilibrium prohibited the run being carried out in the variable-temperature probe, the samples were kept in a thermostated bath of ±0.01° and prior to each measurement the sample was transferred to the nmr probe which was preset to the bath temperature.

Concentrations of trans and cis isomers were determined by

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