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Substitution Reactions of Oxalato Complex Ions. 12. Kinetics of the Anation of Diaquobis(ethylenediamine)cobalt(III) Ion by Oxalate in Aqueous Acidic Solution. Nitrate Ion Catalysis of a Cobalt(III) Substitution Reaction[1,2]

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This study effectively substantiates data obtained previously in a 2.0 M nitrate medium and confirms that the rate of reaction exhibits a strong positive nitrate ion concentration dependence. However, an extension of the study to mixed nitrate/perchlorate media shows that the latter species is essentially inert, except for a rather small general ionic strength effect. The nitrate-catalyzed reaction is best explained in terms of a nitrate-ion-assisted formation of a reactive but stereoretentive five-coordinate intermediate, $Co(en)_2(OH_2)^{3+}$. The residual uncatalyzed reaction takes place according to a conventional dissociative-interchange mechanism involving preassociation of the complex ion and oxalate species. This process has been studied in perchlorate medium at $I = 1.0$ M and over the range of 0.05 M ≤ [oxalate] ≤ 0.25 M and 0.01 M ≤ [H$^+$] ≤ 1.0 M. The extent of the reactant pairing is kinetically identifiable, with equilibrium constant values at 50 °C of 1.0 ± 0.3 and 4.4 ± 1.5 M^{-1} for the association constants of the complex ion with $H_2C_2O_4$ and $HC_2O_4^-$, respectively. The rate constants for the corresponding interchange reactions at 50 °C are identical within experimental error, as are the temperature parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ with average values of $(5.9 \pm 1.8) \times 10^{-5}$ s^{-1}, 27.2 ± 1.5 kcal mol^{-1}, and 6.1 ± 4.5 cal deg^{-1} mol^{-1}, respectively.

Introduction

In earlier studies[2,4,5] kinetic data have been reported for the anation of $Co(NH_3)_5OH_2^{3+}$ by a series of carboxylic acids, including formic, acetic, propionic, oxalic, and malonic acids, and their corresponding carboxylate ions in aqueous acidic solution with nitrate as the excess neutral salt. A common feature found for these systems is the linearity of plots of k_{obsd} vs. [carboxylic acid] under conditions where the carboxylic acids are the only anating species, such that no formation constants for reactant pairing could be determined kinetically. Furthermore, at higher pH where the carboxylate ions are the anating species, the plots of k_{osbd} vs. [carboxylate ion] all deviate from linearity, and reasonable estimations of ion-pair formation constants can be made. These values varied between 1.0 and 5.2 M^{-1} at 70 °C for ion pairs between $Co(NH_3)_5OH_2^{3+}$ and singly charged carboxylate ions and between 5.4 and 9.2 M^{-1} at 70 °C for ion pairs between $Co(NH_3)_5OH_2^{3+}$ and doubly charged carboxylate ions. From the magnitude and trend of the interchange rate constants, it was concluded that the anations by carboxylate ions all proceed according to the well-known I_d mechanism.[6,7] A recent independent study[8] of the anation of $Co(NH_3)_5OH_2^{3+}$ by malonic acid, in which perchlorate was the excess neutral salt, confirmed the absence of any meaningful reactant association in this system and yielded rate data in good agreement with that referenced above.

In contrast to these findings, Brown and Harris[9] reported kinetic evidence for strong reactant association in the anation of *cis*-$Co(en)_2(OH_2)_2^{3+}$ by both $H_2C_2O_4$ and $HC_2O_4^-$ ion in nitrate medium. Formation constants of 11 and 100 M^{-1} at 50 °C for the species *cis*-$Co(en)_2(OH_2)_2^{3+}$,$H_2C_2O_4$ and *cis*-$Co(en)_2(OH_2)_2^{3+}$,$HC_2O_4^-$, respectively, were reported. More recently, Stranks and Vanderhoek[10] studied the pressure dependence of this anation reaction under concentration and medium conditions similar to those of Brown and Harris,[9] and they reported kinetic data at normal pressure which are in excellent agreement with the above-mentioned data. It seemed somewhat surprising to us that such a wide discrepancy should be found between such similar complex ions as $Co(NH_3)_5OH_2^{3+}$ and *cis*-$Co(en)_2(OH_2)_2^{3+}$. We have, therefore, reinvestigated the anation of *cis*-$Co(en)_2(OH_2)_2^{3+}$ by oxalic acid and bioxalate ion in both nitrate and perchlorate media. These new data lead us to a reasonable explanation of the above-mentioned discrepancy based on a specific catalytic effect by nitrate ion.

Experimental Section

cis-$[Co(en)_2CO_3]Cl$ was prepared and converted to *cis*-$[Co(en)_2CO_3]ClO_4$ according to standard procedures.[11,12] Acidification of the latter compound gives stable stock solutions of *cis*-$Co(en)_2(OH_2)_2^{3+}$ when stored at 0 °C.[13] The visible and UV absorption spectra[14] are in good agreement with those reported elsewhere.[9,10,15] *cis*-$[Co(en)_2C_2O_4]ClO_4$ was synthesized by heating a solution of *cis*-$Co(en)_2(OH_2)_2^{3+}$ in 2 M $NaClO_4$ with a 50-fold excess of oxalic acid for several hours at 60 °C. The required product is isolated on cooling the reaction mixture, and its visible and UV spectra[16] are in good agreement with those already reported.[9,10] Spectra were recorded on a Cary Model 118 spectrophotometer, and spectral changes during reaction were measured on a Beckman Model DU instrument with a Gilford Model 220 digital readout attachment. The anation reactions were followed at 500 nm in the thermostated (±0.1 °C) cell compartments of the latter instrument, where the increase in absorbance is over 40%.

The reactions were studied in NO_3^- and ClO_4^- medium at either 1.0 or 2.0 M ionic strength. The acidities were attained by additions of HNO_3 and $HClO_4$. No buffer was needed in the low-acid experiments since the oxalate solutions are self-buffering under the chosen experimental conditions. The Co(III) concentration was set at 5×10^{-3} M throughout the investigation. All chemicals used were of reagent grade, and the laboratory-distilled water was further purified by passage through a mixed-bed ion-exchange column. Under the conditions selected, the reactions were all found to go to completion, and the pseudo-first-order plots of $\ln (A_\infty - A_t)$ vs. t, where A_∞ and A_t are the absorbances at infinite time (i.e., of $Co(en)_2C_2O_4^+$) and time t, respectively, were linear for at least 2 half-lives.

Results and Discussion

In our first experiments we performed the anation reactions in 2.0 M HNO_3 and extended the oxalic acid concentration range used in the earlier study[9] to 0.5 M.[17] The values of k_{obsd} are plotted as a function of [oxalic acid] in Figure 1, curve A, and it is seen that the experimental points fall on the same curve as do the earlier data.[9] When it is assumed that the observed curvature is due to reactant pairing, the mechanism consists of the reactions[9]

$$cis\text{-}Co(en)_2(OH_2)_2^{3+} + H_2C_2O_4 \overset{Q_1}{\rightleftarrows} \{cis\text{-}Co(en)_2(OH_2)_2^{3+},H_2C_2O_4\} \xrightarrow{k_1} cis\text{-}Co(en)_2C_2O_4^{+} + 2H_3O^{+} \quad (1)$$

for which $k_{obsd} = k_1Q_1[H_2C_2O_4]/\{1 + Q_1[H_2C_2O_4]\}$. k_1 and Q_1 values of $(1.39 \pm 0.05) \times 10^{-4}$ s^{-1} and 11.5 ± 1.0 M^{-1}, respectively, were calculated from the usual inverse plot of k_{obsd}^{-1} vs. $[H_2C_2O_4]^{-1}$ by using a least-squares program. These

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Table I. Rate Data for the Anation of *cis*-$Co(en)_2(OH_2)_2^{3+}$ by Oxalic Acid as a Function of Medium Composition[c]

		$10^5 k_{obsd}$,[a] s^{-1}					
		$[H_2C_2O_4]$, M					
$[NO_3^-]$, M	$[ClO_4^-]$, M	0.05	0.1	0.2	0.3	0.4	0.5
2.0	0	5.20	7.31	8.90	10.9	11.9	12.4
1.6	0.4	5.12	6.60	7.75	10.1	11.4	11.4
1.2	0.8	5.30	6.84	7.32	7.80	8.10	8.91
0.8	1.2	3.89	4.66	5.31	5.07	5.83	5.87
0.4	1.6	2.98	3.20	3.38	3.45	3.75	4.29
0	2.0	(0.24)[b]	0.47	0.87	1.25	1.53	1.88

[a] Average of two or three determinations. [b] Extrapolated from values at higher $[H_2C_2O_4]$. [c] 50 °C, $[H^+] = 2.0$ M, ionic strength 2.0 M.

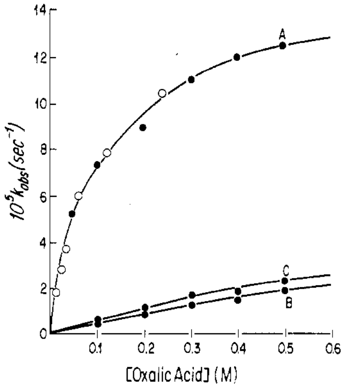

Figure 1. Plot of k_{obsd} vs. [oxalic acid] at 50 °C: A, 2.0 M HNO_3 (○, data reported by Brown and Harris;[9] ●, this work); B, 2.0 M $HClO_4$; C, 1.0 M $HClO_4$/1.0 M $NaClO_4$.

values are in excellent agreement with the corresponding values of 1.4×10^{-4} s^{-1} and 11 M^{-1} obtained by Brown and Harris[9] using similar experimental conditions and a similar method of analysis of the data.

Surprisingly, however, repetition of the above experiments in 2.0 M $HClO_4$ or in a 1.0 M $HClO_4$/1.0 M $NaClO_4$ mixture leads to values for k_{obsd} which are much lower than those found for 2.0 M HNO_3 and show only slight curvature with change in [oxalic acid] (see curves B and C in Figure 1). However, similar isosbestic points and the same reaction products are obtained irrespective of whether a nitrate or perchlorate reaction medium is used. Furthermore, no deviation from linearity in the pseudo-first-order plots or any other information pointing to the possible participation of a long-lived reaction intermediate in either of the reaction media could be detected. Treatment of the data obtained in 2.0 M $HClO_4$ and in 1.0 M $HClO_4$/1.0 M $NaClO_4$ according to the outlined procedure yields identical Q_1 values of 0.8 ± 0.1 M^{-1} and k_1 values of $(6.6 \pm 0.4) \times 10^{-5}$ and $(7.8 \pm 1.3) \times 10^{-5}$ s^{-1}, respectively.

The previously noted enhancement[9] of the rate of anation by nitrate ion was now further examined in a series of experiments in which the total univalent mineral acid concentration (and therefore the ionic strength) was kept constant at 2.0 M, while the anionic partner of the medium was changed incrementally from NO_3^- to ClO_4^-. The results are recorded in Table I, where it is seen that at the higher $[H_2C_2O_4]$ values (e.g., 0.4 and 0.5 M), k_{obsd} increases in an almost linear manner with increasing $[NO_3^-]$. At the lower $[H_2C_2O_4]$ values, however, there is no longer a linear relationship, with k_{obsd} clearly approaching a constant limiting value at the lowest $[H_2C_2O_4]$ (0.05 M). The above behavior suggests that there must be both catalysis and inhibition of the process by nitrate at low $[H_2C_2O_4]$, with the nitrate inhibition effect disappearing at high $[H_2C_2O_4]$.

A variety of plausible reaction mechanisms were tried out, including several which assume formation of nitrate intermediates of various kinds. The most reasonable of these which fulfills the conditions just delineated for the nitrate effect, and which also encompasses the residual nitrate-independent oxalate anation, consists of the conventional I_d reaction scheme of eq 1 supplemented by the nitrate-promoted five-coordinate-intermediate dissociative reaction scheme of eq 2–6. This

$$cis\text{-}Co(en)_2(OH_2)_2^{3+} + NO_3^- \xrightarrow{k_2} Co(en)_2(OH_2)^{3+} + NO_3^- + H_2O \quad (2)$$

$$Co(en)_2(OH_2)^{3+} + NO_3^- \xrightarrow{k_3} cis\text{-}Co(en)_2(OH_2)(NO_3)^{2+} \quad (3)$$

$$Co(en)_2(OH_2)^{3+} + H_2C_2O_4 \xrightarrow{k_4} cis\text{-}Co(en)_2(OH_2)(HC_2O_4)^{2+} + H^+ \quad (4)$$

$$cis\text{-}Co(en)_2(OH_2)(NO_3)^{2+} + H_2O \xrightarrow{\text{fast}} cis\text{-}Co(en)_2(OH_2)_2^{3+} + NO_3^- \quad (5)$$

$$cis\text{-}Co(en)_2(OH_2)(HC_2O_4)^{2+} \xrightarrow[\text{ring closure}]{\text{fast}} Co(en)_2C_2O_4^+ + H_3O^+ \quad (6)$$

mechanism is comparable to that previously proposed[19] for induced aquation of $Co(en)_2N_3Cl^+$ by Hg^{2+} where the Cl^- ligand is "pulled off" to form $HgCl^+$. In the present instance, the H_2O ligand is visualized as being similarly pulled off by NO_3^-, without, however, the formation of any distinguishable NO_3^-,H_2O entity. Retention of configuration is assumed in the above mechanism since the spectral data show no evidence for concurrent cis–trans isomerization of the diaquo parent complex even at low $[H_2C_2O_4]$. The assumption that reaction 5 is relatively rapid is in keeping with the well-known instability of nitrato complexes toward hydrolysis,[7,20] while the rapid ring closure of the monodentate bioxalato species as in reaction 6 has previously been documented.[21]

One can now apply the stationary-state approximation to evaluate the rate law for the nitrate-promoted process, which, when combined with the rate law for the residual interchange scheme of eq 1, yields the additive rate law $k_{obsd} = k_I + k_{NO_3}$, or, in detail:

$$k_{obsd} = \frac{k_1 Q_1 [H_2C_2O_4]}{1 + Q_1[H_2C_2O_4]} + \frac{k_2 k_4 [NO_3^-][H_2C_2O_4]}{k_3[NO_3^-] + k_4[H_2C_2O_4]} \quad (7)$$

The assumption that k_I is essentially independent of the total perchlorate content of the medium is supported by comparing the figures quoted above for k_1 and Q_1 in 2.0 M perchlorate with those reported later for 1.0 M perchlorate (see Table II). The general ionic properties of the medium should remain unchanged whether the anion is NO_3^- or ClO_4^-, since these species carry identical charges and are of similar volume. A quantitative test of eq 7 can be made by recasting it in the form

$$\frac{[H_2C_2O_4]}{k_{obsd} - k_I} = \frac{k_3}{k_2 k_4} + \frac{[H_2C_2O_4]}{k_2[NO_3^-]} \quad (8)$$

The values of k_I are known at each $[H_2C_2O_4]$ either by

Table II. Rate Data for the Anation of *cis*-$Co(en)_2(OH_2)_2^{3+}$ by Oxalic Acid/Bioxalate Ion as a Function of Temperature, [Total Oxalate], and [H^+] in Perchlorate Medium[a]

[H^+], M	[total oxalate], M	$10^5 k_{obsd}$, s^{-1} 50 °C	60 °C	70 °C
1.0	0.25	1.12	3.77	10.9
	0.20	0.93	3.18	9.83, 9.71
	0.15	0.75, 0.74	2.72, 2.58	6.87, 7.48
	0.10	0.53, 0.53	1.82, 1.71	5.13
	0.05	0.26, 0.28	0.86, 0.98	2.60
0.5	0.25	1.37, 1.19	3.92	11.2, 11.9, 11.8, 12.0
	0.20	1.16, 1.27	3.56, 3.45	12.1, 10.9
	0.15	0.91, 0.74, 1.04, 1.05	2.82	9.18
	0.10	0.56, 0.59, 0.68	1.99	6.07
	0.05	0.32, 0.34	0.98	2.90
0.1	0.25	1.95, 2.18	6.97	19.6
	0.20	1.72, 2.00	6.03	18.8
	0.15	1.31, 1.50	4.82	15.9
	0.10	1.01, 1.10	3.56	10.7
	0.05	0.56, 0.63	1.88	5.55
0.05	0.10	1.20	4.53	12.6, 11.6
	0.05	0.76	2.34	6.51
0.01	0.05	1.07	3.30	11.4, 11.7, 12.0

[a] Ionic strength 1.0 M.

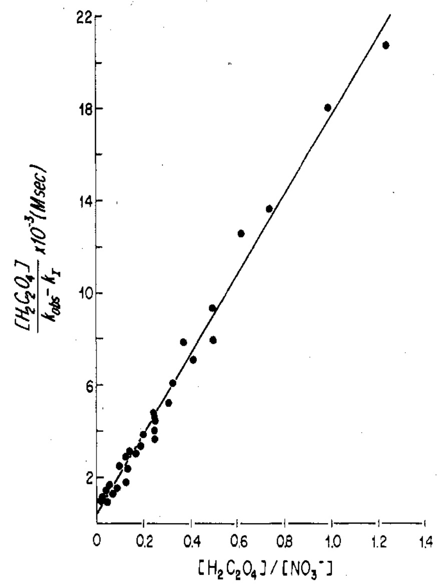

Figure 2. Plot of $[H_2C_2O_4]/(k_{obsd} - k_I)$ vs. $[H_2C_2O_4]/[NO_3^-]$ at 50 °C and [H^+] = 2.0 M.

calculation from the known values of k_1 and Q_1 at 50 °C and $I = 2.0$ M as already determined or by direct use of the values of k_{obsd} in absence of nitrate as given in the last row of Table I. One can therefore plot the left-hand side of eq 8 vs. the ratio $[H_2C_2O_4]/[NO_3^-]$, which should yield a straight line. The excellence of this fit to the data is demonstrated in Figure 2, and least-squares analysis, with a correlation coefficient of 0.993, leads to the values $k_2 = (5.9 \pm 0.1) \times 10^{-5}$ M^{-1} s^{-1} and $k_3/k_4 = (2.1 \pm 0.9) \times 10^{-2}$.

It is particularly significant that $H_2C_2O_4$ is ~50 times more effective as a nucleophile than is NO_3^-, in spite of the latter's negative charge. This considerable variation in nucleophilicity suggests that the five-coordinate intermediate of the nitrate-catalyzed process is relatively stable and will show little tendency to "pick up" ligand water directly in the presence of more effective nucleophiles.[22] We are therefore justified in our exclusion of such a step in our proposed mechanism. The other noteworthy feature of the kinetic data is that k_2 is significantly larger than the second-order rate constant for solvent water exchange with *cis*-$Co(en)_2(H_2O)_2^{3+}$ in perchlorate medium[23] (7.5×10^{-6} M^{-1} s^{-1} at 50 °C). In fact, catalysis of water exchange by anions has been previously observed in studies[24] of $Cr(H_2O)_6^{3+}$. For this, NO_3^- is somewhat more effective than ClO_4^-, but both effects were ascribed to normal ionic strength factors, rather than to specific anion interaction effects. However, in a recent study[25] of the replacement of water by dimethyl sulfoxide in the coordination shell of $Cr(H_2O)_5NO_3^{2+}$, it was found that the nitrato complex is more than 10^5 times more labile than is $Cr(H_2O)_6^{3+}$ under the same conditions. A similar labilization had been previously observed[26] for the ammonia dissociation reactions of $Cr(NH_3)_5NO_3^{2+}$ as compared to those of $Cr(NH_3)_6^{3+}$. Clearly, the nitrate ion has some unusually specific labilization properties when within the ligand grouping of hexacoordinate chromium(III), so at least a modest effect might be expected even when it is external to a hexacoordinate cobalt(III) species, as found in the present study. It is of interest in this connection that Kallen reports[27] a significant nitrate-induced enhancement of the anation of *cis*-diaquobis(oxalato)chromate(III) by oxalate, with the same linear relationship found in our present study at high [oxalate]. However, it should be noted that the oxalate anation reactions of $Co(NH_3)_5OH_2^{3+}$ and others of the same type[2,4,5,8] are *not* catalyzed by nitrate, nor does the nitrato complex $Co(NH_3)_5NO_3^{2+}$ show any unusual dissociative properties other than its previously referenced[7,20] ease of substitution of water for nitrate. It was previously suggested[9] that the "nitrate effect" in $Co(en)_2(OH_2)_2^{3+}$ oxalate anation results from specific labilization of the water ligand cis to the one assumed to be associated with the entering oxalate group, suggesting a consistently linear relationship between k_{obsd} and [NO_3^-] under all conditions. We now modify this view as described above to include competition between oxalate and nitrate for the reactive $Co(en)_2OH_2^{3+}$ moiety, though with oxalate much favored, such that at high values of [$H_2C_2O_4$] a linear k_{obsd} vs. [NO_3^-] plot is indeed observed. Alternative explanations include catalysis by trace concentrations of nitric acid decomposition products, such as HNO_2, $H_2NO_2^+$, and NO^+, as suggested in other studies.[20,28-30] Whatever the nature of such a catalytic agent, its concentration and reactivity must be highly reproducible over a wide range of conditions, as is obvious by comparison of the present data with that of earlier workers.[9,10]

We now turn to the results of an expanded kinetic study of the anation of *cis*-$Co(en)_2(OH_2)_2^{3+}$ by $H_2C_2O_4$ and $HC_2O_4^-$ ion in perchlorate medium. Due to the low solubility of sodium oxalate in perchlorate medium, especially at lower acidity, the ionic strength of the solutions was decreased to 1.0 M. The values of k_{obsd} as a function of [total oxalate], [H^+], and temperature are recorded in Table II. Solubility of oxalate and isomerization/deprotonation of the *cis*-$Co(en)_2(OH_2)_2^{3+}$ species,[13] limit the extension of the data in Table II to lower [H^+].[31] Plots of k_{obsd} vs. [total oxalate] deviate more from linearity at lower [H^+], pointing toward the stronger ion-pair formation with bioxalate ion. The suggested reaction mechanism consists of the reactions in (1) with the addition of (9) to account for the data in the less acidic media:

$$cis\text{-}Co(en)_2(OH_2)_2^{3+} + HC_2O_4^- \overset{Q_9}{\rightleftharpoons} \{cis\text{-}Co(en)_2(OH_2)_2^{3+},HC_2O_4^-\} \xrightarrow{k_9} cis\text{-}Co(en)_2C_2O_4^+ + H_3O^+ + H_2O \quad (9)$$

For such a system the all-inclusive rate law is[4,5,8]

$$k_{obsd} = -d \ln [Co(en)_2(OH_2)_2^{3+}]/dt = \frac{k_1Q_1[H_2C_2O_4] + k_9Q_9[HC_2O_4^-]}{1 + Q_1[H_2C_2O_4] + Q_9[HC_2O_4^-]} \quad (10)$$

Table III. Rate and Activation Parameters for the Anation of *cis*-$Co(en)_2(OH_2)_2{}^{3+}$ by Oxalic Acid and Bioxalate Ion in Perchlorate Medium[a]

temp, °C	$[H^+]$, M	10^5k_1, s^{-1}	Q_1, M^{-1}	10^5k_9, s^{-1}	Q_9, M^{-1}
50	1.0	5.9 ± 1.7	1.0 ± 0.3	5.8± 0.5	4.4 ± 1.5
	0.5	5.9 ± 2.6	1.2 ± 0.5		
60	1.0	24 ± 18	0.8 ± 0.6	20 ± 1	4.2 ± 0.8
	0.5	24 ± 8	0.8 ± 0.3		
70	1.0	76 ± 22	0.7 ± 0.2	73 ± 11	3.5 ± 2.9
	0.5	79 ± 35	0.8 ± 0.3		
$\Delta H^\ddagger$, kcal mol^{-1}		27.4 ± 1.3		27.0 ± 0.8	
$\Delta S^\ddagger$, cal deg^{-1} mol^{-1}		+6.7 ± 3.8		+5.5 ± 2.5	

[a] Ionic strength 1.0 M.

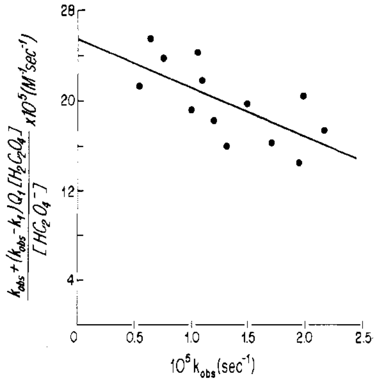

Figure 3. Plot of $\{k_{obsd} + (k_{obsd} - k_1)Q_1[H_2C_2O_4]\}/[HC_2O_4^-]$ vs. k_{obsd} at 50 °C, $0.01 \leq [H^+] \leq 0.1$ M, and $I = 1.0$ M (ClO_4^-).

At $[H^+] \geq 0.5$ M, where the oxalate can be assumed to be entirely protonated,[17] this rate law simplifies to the one already defined, viz. $k_{obsd} = k_1Q_1[H_2C_2O_4]/(1 + Q_1[H_2C_2O_4])$, and was utilized as before to evaluate k_1 and Q_1. These values are recorded in the first columns of Table III, together with the corresponding activation parameters. It is noted that, as expected, the constants obtained in 0.5 and 1.0 M acid are identical within experimental error. Neither do they differ significantly from the values obtained at $I = 2.0$ M in perchlorate medium mentioned above, in keeping with expectation for an ion/molecule reaction.

The data at lower $[H^+]$ can now be employed to evaluate k_9 and Q_9 by making use of the k_1 and Q_1 values in 1.0 M $HClO_4$ given in Table III. This is accomplished by rewriting eq 10 in the form

$$\frac{k_{obsd} + (k_{obsd} - k_1)Q_1[H_2C_2O_4]}{[HC_2O_4^-]} = k_9Q_9 - Q_9k_{obsd} \qquad (11)$$

Thus, a plot of the left-hand side of eq 11 vs. k_{obsd} should yield a straight line from with k_9 and Q_9 can be derived. An example of such a plot for one set of conditions appears in Figure 3, and the results of this analysis, together with the corresponding activation parameters, are recorded in the last two columns of Table III.

The values of k_1 and k_9 are seen to be very close to one another at each temperature and turn out to be ~0.15 times as great as the water-exchange rate constant.[21] Moreover, both sets of activation parameters are very close to one another and also to those for water exchange ($\Delta H^\ddagger = 28.8$ kcal mol^{-1}; $\Delta S^\ddagger = +15$ eu).[21] These observations can be taken as evidence for a dissociative interchange (I_d) mechanism, as concluded earlier[2,4,5] in the studies of the anation of $Co(NH_3)_5OH_2{}^{3+}$. Both Q_1 and Q_9 show slight decreases with an increase in temperature in accord with similar findings discussed in detail elsewhere,[32] and the magnitudes are in good agreement with predictions from simple Coulombic force field calculations.[33] Our inability to obtain evidence for preassociation of reactants in the anation of $Co(NH_3)_5(OH_2)^{3+}$ by oxalic and other carboxylic acids suggests that there may indeed be a special type of interaction between the cis diaquo group of *cis*-$Co(en)_2(OH_2)_2{}^{3+}$ and oxalic acid, perhaps through hydrogen bonding as previously suggested, but not nearly so effectively as then believed.[9] The value of Q_9, however, lies well within the range of values reported for $Co(NH_3)_5OH_2{}^{3+}$/carboxylate ion pairs.

In conclusion, it can now be stated decisively that the discrepancy discussed in the Introduction is the result of a specific nitrate ion effect. The fact is that the species $Co(NH_3)_5OH_2{}^{3+}$ and *cis*-$Co(en)_2(OH_2)_2{}^{3+}$ do exhibit very similar kinetic behavior during anation by carboxylic acids and carboxylate ions, provided the medium is really "inert", as is apparently true for perchlorate.

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Registry No. *cis*-$Co(en)_2(OH_2)_2{}^{3+}$, 21247-59-6; $H_2C_2O_4$, 144-62-7; $HC_2O_4^-$, 920-52-5; NO_3^-, 14797-55-8.

References and Notes

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(16) Maxima occur at 495 and 352 nm, with ε 113.5 and 145.3 M^{-1} cm^{-1}, respectively.
(17) We have adopted a value of 0.06 for the first acid dissociation constant K_1 of oxalic acid over the entire temperature range of this study. Some temperature variation is observed in this constant in the 50–80 °C range (see ref 9 and 18 and other references quoted therein), but it is not significant to our conclusions. At $[H^+] = 1.0$ and 2.0 M, virtually all oxalate species exist as oxalic acid, such that $[H_2C_2O_4]$ = [total oxalate].
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Role of Coordinated Hydroxide Ion in Configurational Conversions of Tetraamine Macrocyclic Ligand Complexes of Copper(II)

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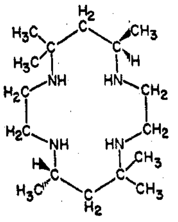
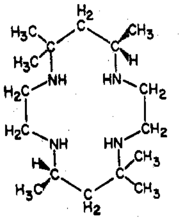
Blue-to-red interconversion of the copper(II) complex of tet b (II) is base catalyzed due to the required inversion of nitrogen atoms in the complexes. Coordinated hydroxide ion is much more reactive than free hydroxide ion and a concerted mechanism is proposed in which intramolecular hydrogen bonding, nitrogen inversion, and ring conformational changes occur.

Introduction

The macrocyclic ligand 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane exists as two isomers, tet a (I) and tet b (II).[2,3] Each of these isomers forms a blue complex



I



II

as well as red complexes with copper(II).[4,5] The present paper concerns the kinetics of the blue-to-red interconversion of $[Cu(tet\ b)]^{2+}$ (eq 1) and the important contribution of the

$$[Cu(tet\ b)(blue)]^{2+} \rightarrow [Cu(tet\ b)(red)]^{2+} \qquad (1)$$

coordinated hydroxide ion in the reaction, where inversions of the nitrogen atoms are required. The blue-to-red reaction is much faster than the rates of dissociation of the macrocyclic ligands from copper(II).[5] Hence there is no doubt that the configurational conversion occurs while the ligand is coordinated. In this reaction structures have been determined for crystalline forms of the reactant[6] and of the product.[7] Therefore, it is possible to be quite specific about the rearrangements which accompany the color change with $[Cu(tet\ b)]^{2+}$. The blue tet b complex has been isolated as $[Cu(tet\ b)]_2Cl(ClO_4)_3$ which contains five-coordinate (trigonal-bipyramidal) copper as shown in Figure 1. The ligand is in its most stable, folded configuration with both six-membered chelate rings in a symmetrical chair form and both five-membered chelate rings in a gauche form.[6] Chloride ion, which occupies one of the positions in the trigonal plane, dissociates from the copper in dilute solution but the electronic spectral characteristics of the complex in aqueous solution are similar to those of the crystals.[8]

The structure of $[Cu(tet\ b)(red)](ClO_4)_2$ is shown in Figure 2.[7] The copper is four-coordinate with a very slightly distorted square-planar arrangement of the four nitrogens of tet b. The six-membered chelate rings are in the chair form but the five-membered chelate rings are in an eclipsed (or partially eclipsed) form rather than the gauche form. The diagrams of structures III and IV in Figures 1 and 2 indicate the relative positions of the hydrogen atoms on the four nitrogens. It can be seen that two of the four nitrogens must be inverted during the blue-to-red reaction. Inversion reactions of uncomplexed amines have been studied extensively[9] and a few reactions of various polyamine complexes with the metal ions Co(III),[10,16] Pt(II),[11] Pt(IV),[12] Pb(II),[13] Ni(II),[14,15] and Cu(II)[14] have been investigated. It is not surprising that hydroxide ion assists the inversion reaction in eq 1, but it is most interesting that the main reaction pathway is via hydroxide ion which is coordinated to the copper. Poon and Tobe[16] studied the cis to trans isomerization of *cis*-$[Co(cyclam)Cl_2]^+$ in aqueous solution and also suggested an intramolecular proton transfer from nitrogen to oxygen in the *cis*-$[Co(cyclam)(OH)(H_2O)]^{2+}$ cation.

Table I. Visible and Near-Infrared Absorption Bands

complex	λ_{max}, nm	ϵ_{max}, $M^{-1}\ cm^{-1}$
$[Cu(tet\ b)(red)]^{2+}$	525	174
$[Cu(tet\ b)(blue)]^{2+}$	833	269
	680 sh	172
$[Cu(tet\ b)Cl(blue)]^{2+}$	840	324
	670	316

Experimental Section

Reagents. The macrocyclic ligand tet b was prepared by using the procedure described by Hay, Lawrance, and Curtis.[17] $\{[Cu(tet\ b)]_2Cl\}(ClO_4)_3$ was prepared by using the procedure described by Bauer.[6] Anal. Calcd for $2CuC_{16}H_{36}N_4{\cdot}Cl{\cdot}3ClO_4$: C, 37.32; H, 7.07; Cl, 13.77. Found: C, 37.22; H, 7.12; Cl, 13.63. $[Cu(tet\ b)(red)](ClO_4)_2$ was prepared by the procedure given by Bauer.[8] Anal. Calcd for $CuC_{16}H_{36}N_4{\cdot}2ClO_4$: C, 35.14; H, 6.63; Cl, 12.96. Found: C, 35.05; H. 6.84; Cl, 13.10. All other chemicals used in this work were of GR grade of Merck.

Instrumentation. A Cary 17 spectrophotometer with a thermostated cell compartment was used to measure absorption spectra and to follow the reactions. A Durrum D-115 stopped-flow spectrophotometer was used to measure the absorbance jump after stopped-flow mixing of base with $[Cu(tet\ b)(blue)]^{2+}$ solutions. For pH measurements, a Radiometer PHM 64 equipped with a GK 2401 B combined electrode was used. The pH was standardized with NBS buffers, and the readings were corrected to give the hydroxide ion concentration. The hydroxide ion concentration in 0.1 M $NaNO_3$ solution is calculated from $K_w = 10^{-13.78}$ and $-\log[H^+] = pH - 0.11$. Above pH 13, standard NaOH was used to give the hydroxide ion concentration. The rate constants and stability constants were obtained by a linear least-squares fit of the data by using the IBM 1130 computer.

Kinetic Measurements. All reactions were measured at 840 nm and studied under conditions which were first order in the blue form

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