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Kinetics and Mechanism of Aquation and Formation Reactions of *cis*-Carbonatobis(oxalato)chromate(III) Ion in Aqueous Solution[1]

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The title compound has been prepared and characterized for the first time. The kinetics of the aquation and formation reactions of this carbonato complex were studied by stopped-flow spectrophotometry. The acid catalysis reactions were studied in the range of $2 > [H^+] > 0.01$ M and $10 < T < 25$ °C at an ionic strength of 2 M ($NaClO_4$). Only the ring-opening reaction of $Cr(CO_3)(ox)_2^{3-}$ is observed, $k = 2.04$ M^{-1} s^{-1} at 25 °C, as subsequent decarboxylation is too fast to measure even at 2 M hydrogen ion concentration. Carbon dioxide uptake by *cis*-diaquobis(oxalato)chromate(III) was investigated over the ranges $7.01 < pH < 9.34$ and $10 < T < 25$ °C at an ionic strength of 0.5 M (NaCl). The major reactant species in the pH range studied was *cis*-$Cr(ox)_2(OH)(OH_2)^{2-}$ which takes up CO_2 to form *cis*-$Cr(ox)_2(HCO_3)(OH_2)^{2-}$. Subsequently, slower ring closure of the latter species to form the carbonato chelate is observed. The results are compared to those of cobalt complexes previously studied and the possible mechanisms are discussed.

Introduction

It is well documented[3] that the acid-catalyzed aquation of chromium–ammine complexes, viz., CrN_5X^{2+} or $CrN_4X_2^+$, where N represents an ammine group and X is the monovalent replaceable ligand, is generally complicated by concurrent Cr–N bond fission. However, if the ammine groups are replaced by O-donating ligands, e.g., oxalate or malonate, substitution of the relatively labile group X^- takes place without any side reactions.[4] In continuing our studies on carbonato complexes of various transition-metal ions[5-7] we have recently started work on carbonato complexes of chromium(III). For the reason stated above we have failed to prepare carbonatoamminechromium(III) complexes. We found that the Cr–N bonds break rapidly before any measurable association takes place[8] between the hydroxide of hydroxoamminechromium(III) and carbon dioxide. Apparently this problem does not arise when the ammine ligands are replaced by oxalate groups. In this paper we report the preparation and characterization of the potassium salt of carbonatobis(oxalato)chromate(III) (the oxalato ligand will be hereafter represented by ox) and the results of a detailed kinetic investigation of the aquation and formation of this complex.

Experimental Section

The cis form of potassium diaquobis(oxalato)chromate(III) dihydrate was prepared by the method of Werner.[10] Its composition was confirmed by microanalysis, and the visible–UV spectrum agreed closely with that given in the literature.[11]

Potassium carbonatobis(oxalato)chromate(III) trihydrate was prepared by gradually adding solid K_2CO_3 (ca. 40 mg in 10 cm^3 of water) to a stirred solution containing 1 g of *cis*-$K[Cr(ox)_2(OH_2)_2]\cdot 2H_2O$ in 10 cm^3 of water until a pH of ca. 8.5 was attained. After the solution was stirred for 10 min, it was cooled in an ice bath and ethanol was added until a green precipitate was formed. The crystals were filtered off and thoroughly washed with ethanol, followed by ether. The purity of the complex was checked by microanalysis.[12] Anal. Calcd for $K_3[Cr(CO_3)(C_2O_4)_2]\cdot 3H_2O$: K, 25.8; C, 13.07; H, 1.32; Cr, 11.4. Found: K, 26.1; C, 13.07; H, 1.32; Cr, 11.0. All other chemicals used were of reagent grade, and deionized, doubly distilled water was used in preparing all solutions.

The visible and UV spectra of the various complex species of significance to this research are shown in Figure 1. These were obtained at room temperature using a Zeiss DMR10 recording spectrophotometer.

The infrared spectrum of $K_3[Cr(CO_3)(ox)_2]\cdot 3H_2O$ shows a very weak band at 1025 cm^{-1} which compares with the reported[13] C–O stretching frequencies at 1593, 1030, and 765 cm^{-1} for a series of carbonatocobalt(III) complexes. However the remaining C–O frequencies of the carbonate are undoubtedly masked by the strong bands of the oxalate ligands.

Kinetics. The acid hydrolysis of $Cr(CO_3)(ox)_2^{3-}$ was investigated using an Aminco stopped-flow spectrophotometer equipped with a Dasar data storage system. The reaction was followed at 300 nm where the absolute absorbance difference between the carbonato complex and the aquated product is maximal (see Figure 1). The hydrogen ion concentration was regulated with $HClO_4$ and the ionic strength was kept at 2 M using sodium perchlorate.

The kinetics of CO_2 uptake by diaquobis(oxalato)chromate(III) were studied by the "acidification technique"[9] using the abovementioned stopped-flow equipment. The reaction was monitored at 263 nm, where there is a maximum difference in molar absorptivities between the hydroxoaquo or dihydroxo species and the carbonato species. A Tris base–Tris hydrochloride buffer[14] was used to control the pH of the reaction mixture. The ionic strength of these solutions was maintained at 0.5 M (NaCl). It should be noted that $NaClO_4$ interferes with the function of the buffer. All pH measurements were made using either a Beckman Research Model or a Radiometer 64 pH meter.

Complex concentrations were maintained at 10^{-3} M throughout this study.

The absorbance–time data were transferred to computer punchtapes by means of a teletype connected to the Dasar system, and the rate constants were then computed using a standard least-squares program.

p*K* Determination. The acid dissociation constants K'_1 and K'_2 of *cis*-$Cr(ox)_2(OH_2)_2^-$ were determined at 10, 15, 20, and 25 °C by titrating a diaquo complex solution (4×10^{-3} M) with 0.1 M NaOH solution. The ionic strength of these solutions was maintained at 0.5 M with NaCl. The K'_1 and K'_2 values so obtained are recorded in Table IV.

Results and Discussion

The pseudo-first-order rate constants for the acid hydrolysis of $Cr(CO_3)(ox)_2^{3-}$ at four temperatures are summarized in Table I, together with their standard deviations. Linear regressional analysis of these data[15] shows that the rate constants are linear with $[H^+]$ over the entire range of concentration studied (0.01–2.0 M). Kinetic runs at hydrogen ion concentrations lower than 0.01 M were abandoned because of concurrent hydrolysis of the oxalate ligands and also because of interaction of the buffer with the substrate.

These results could be satisfactorily interpreted in terms of the mechanism previously proposed for the acid hydrolysis of various anionic and cationic cobalt(III) carbonato complexes[16-18] and can be expressed as

$$Cr(CO_3)(ox)_2^{3-} + H_2O \xrightarrow{k_0} Cr(ox)_2(HCO_3)(OH)^{3-} \tag{1}$$

$$Cr(CO_3)(ox)_2^{3-} + H_3O^+ \xrightarrow{k_1} Cr(ox)_2(HCO_3)(OH_2)^{2-} \tag{2}$$

$$Cr(ox)_2(HCO_3)(OH_2)^{2-} \xrightarrow{k_2} Cr(ox)_2(OH)(OH_2)^{2-} + CO_2 \tag{3}$$

$$\begin{aligned} &Cr(ox)_2(HCO_3)(OH_2)^{2-} + H_2O \overset{K'_3}{\rightleftharpoons} \\ &\quad Cr(ox)_2(HCO_3)(OH)^{3-} + H_3O^+ \end{aligned} \tag{4}$$

$$Cr(ox)_2(OH_2)_2^- + H_2O \overset{K'_1}{\rightleftharpoons} Cr(ox)_2(OH)(OH_2)^{2-} + H_3O^+ \tag{5}$$

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Table I. Pseudo-First-Order Rate Constants for the Acid Hydrolysis of *cis*-Carbonatobis(oxalato)chromate(III), $I = 2.0$ M ($NaClO_4$)

	$10^2 k_{obsd}$, s^{-1}			
$[H^+]$, M	10 °C	15 °C	20 °C	25 °C
2.0	124 ± 6	162 ± 4	272 ± 9	520 ± 32
1.8	106 ± 8	147 ± 5	262 ± 11	445 ± 19
1.6	86.1 ± 1.3	135 ± 3	229 ± 8	438 ± 31
1.4	81.8 ± 1.8	115 ± 3	195 ± 6	385 ± 32
1.2	68.1 ± 0.5	96.6 ± 5.8	146 ± 13	256 ± 9
1.0	49.8 ± 1.9	84.8 ± 2.6	125 ± 8	208 ± 5
0.75	41.5 ± 0.9	56.4 ± 1.4	92.5 ± 4.1	131 ± 4
0.50	25.3 ± 0.5	46.8 ± 5.2	74.4 ± 6.4	
0.45				101 ± 2
0.40	19.6 ± 0.4	40.4 ± 0.8	49.6 ± 4.8	
0.30	12.5 ± 0.2	18.2 ± 0.5	34.5 ± 1.5	52.4 ± 0.3
0.20		15.0 ± 1.6	22.6 ± 0.2	45.2 ± 2.4
0.15		9.36 ± 0.16		19.9 ± 0.5
0.10		8.56 ± 0.52	10.2 ± 0.6	18.8 ± 0.9
0.075	3.46 ± 0.09	4.96 ± 0.08	7.88 ± 0.56	10.2 ± 2.4
0.050		4.20 ± 0.12	5.24 ± 0.44	8.80 ± 0.16
0.025	1.18 ± 0.04	1.78 ± 0.06	2.42 ± 0.11	4.40 ± 0.28
0.020	0.856 ± 0.004	1.41 ± 0.03	2.21 ± 0.08	3.99 ± 0.06
0.010	0.484 ± 0.024	0.944 ± 0.152	1.28 ± 0.02	1.31 ± 0.05

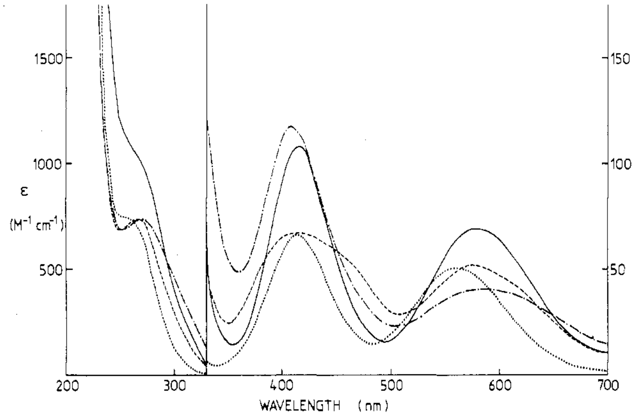


Figure 1. Visible and UV absorption spectra of the complexes: ···, *cis*-$Cr(ox)_2(OH_2)_2^-$; ---, *cis*-$Cr(ox)_2(OH)(OH_2)^{2-}$; -·-, *cis*-$Cr(ox)_2(OH)_2^{3-}$; —, $Cr(CO_3)(ox)_2^{3-}$.

According to this reaction sequence the expected rate expression should be $k_{obsd} = k_0 + k_1[H^+]$. However the k_0 values are too small to be observed in the range of acid concentration studied.[19] Hence the rate expression reduces to $k_{obsd} = k_1[H^+]$. The k_1 values, obtained using a "best fit" program, yielded the activation parameters $\Delta H^{\ddagger} = 14.7 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -8 \pm 2$ cal deg^{-1} mol^{-1}.

From the mechanism proposed above it is clear that the k_{obsd} values should increase linearly with $[H^+]$ and then start to level off to a constant value at high acidity. This constant value should represent the rate constant for decarboxylation of the aquobicarbonato species, k_2 in eq 3. The data in Table I clearly show that even at 2 M $[H^+]$ there is no indication of leveling off. This immediately suggests that the rate of decarboxylation of the aquobicarbonato species is much faster than the rate of ring opening. Since decarboxylation occurs by carbon–oxygen bond fission, the reactivity is not expected to be dependent on the nature of the metal.[5] Assuming a decarboxylation rate constant (k_2) for $Cr(ox)_2(HCO_3)(OH_2)^{2-}$ of ca. 55 s^{-1} [18] and knowing the ring-opening rate constant (k_1) is 2.04 M^{-1} s^{-1}, then at 2 M $[H^+]$, $k_{obsd} = 4.08$ s^{-1}. Thus, at the highest acid concentration studied, k_2 is nearly 14 times greater than k_1, which justifies our experimental observation.

It is of interest to compare the rate parameters for the acid-catalyzed ring-opening process of $Cr(CO_3)(ox)_2^{3-}$ with those of various anionic carbonatocobalt(III) complexes. These data are shown in Table II. It is obvious that the overall charge on the complex ion is not a significant factor in determining the rate of reaction. As proposed earlier,[18] the relative magnitudes of the rate constants appear to depend on the stereochemical requirements of the "inert" ligands. Thus stereochemical reorganization, as well as solvation properties, reflect in the activation parameters. The nature of the central metal atom should not be a prime factor in determining the reactivity, since the rates of aquation of Cr(III) complexes do not differ very much from those of the Co(III) complexes, although the substitution reactions of the former complexes are believed to occur by an I_a mechanism.[21]

Table II. Rate Parameters for the Acid-Catalyzed Ring Opening of Some Anionic Chelated Cobalt(III) and Chromium(III) Carbonato Complexes at 25 °C, $I = 2.0$ M

Complex ion	k_1, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	Ref
$Co(CO_3)(NTA)^{2-}$	42	16	−2	16
α-$Co(CO_3)(EDDA)^-$	118	12	−8	17
β-$Co(CO_3)(EDDA)^-$	2.4	11	−20	17
$Co(CO_3)(gly)_2^-$	8.0	22	+20	20
$Cr(CO_3)(ox)_2^{3-}$	2.0	14.7	−8	This work

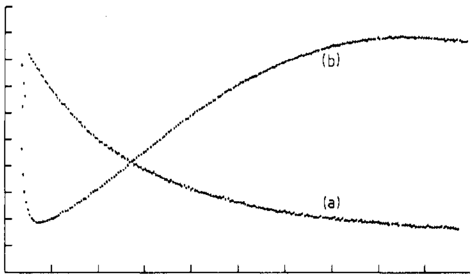


Figure 2. Oscilloscopic traces for CO_2 uptake by *cis*-$Cr(ox)_2(OH)(OH_2)^{2-}$ at pH 8.20 and 25 °C with $[CO_2] = 0.01$ M. The ordinate is in % transmission, while the abscissa is calibrated at (a) 0.1 s/division and (b) 2 s/division.

Stopped-flow traces for the CO_2 uptake by *cis*-$Cr(ox)_2(OH)(OH_2)^{2-}$ clearly show the existence of two kinetically distinguishable successive reactions, as can be seen in Figure 2. The initial rapid rate corresponds to the formation of a monodentate carbonato species (Figure 2a). The trace in Figure 2b then represents the relatively slow ring closure of the coordinated carbonate. These results are entirely consistent with previous studies of CO_2 uptake by hydroxoaquocobalt(III) complexes.[6,7]

The CO_2 uptake study was conducted in the ranges 10 < temperature < 25 °C and 7.01 < pH < 9.34, and the resulting pseudo-first-order rate constants are recorded in Table III.

Table III. Rate Constants[a] for the Carbon Dioxide Uptake by $Cr(ox)_2(OH_2)_2^-$

10 °C		15 °C		20 °C		25 °C	
pH	$10k'_{obsd}$	pH	$10k'_{obsd}$	pH	$10k'_{obsd}$	pH	$10k'_{obsd}$
7.22	2.41 ± 0.07	7.26	2.62 ± 0.24	7.01	5.28 ± 0.09	7.04	5.72 ± 0.39
7.23	2.00 ± 0.01	7.33	2.67 ± 0.14	7.10	3.97 ± 0.08	7.09	7.77 ± 0.04
7.25	1.57 ± 0.06	7.36	2.43 ± 0.13	7.17	4.43 ± 0.10	7.18	6.90 ± 0.31
7.36	1.77 ± 0.04	7.41	2.76 ± 0.06	7.25	4.47 ± 0.06	7.31	4.82 ± 0.09
7.42	2.16 ± 0.04	7.48	3.14 ± 0.49	7.34	4.87 ± 0.20	7.40	5.71 ± 0.08
7.58	2.47 ± 0.07	7.49	2.51 ± 0.24	7.40	5.10 ± 0.12	7.46	7.97 ± 0.17
7.68	2.56 ± 0.05	7.53	3.08 ± 0.34	7.43	5.14 ± 0.15	7.78	8.58 ± 0.25
7.69	2.30 ± 0.06	7.60	2.95 ± 0.07	7.52	4.76 ± 0.20	7.85	4.49 ± 0.09
7.77	1.67 ± 0.03	7.65	3.55 ± 0.48	7.56	4.98 ± 0.09	7.92	3.96 ± 0.05
7.78	1.93 ± 0.05	7.68	2.36 ± 0.06	7.60	4.92 ± 0.09	8.03	7.08 ± 0.24
7.90	1.32 ± 0.04	7.76	2.96 ± 0.06	7.71	4.48 ± 0.15	8.04	9.47 ± 0.27
8.58	0.87 ± 0.03	7.90	2.78 ± 0.10	7.97	6.63 ± 0.20	8.20	6.07 ± 0.19
8.79	0.79 ± 0.02	7.95	1.98 ± 0.05	9.18	5.66 ± 0.26	8.22	3.63 ± 0.60
9.34	0.89 ± 0.04	8.12	2.93 ± 0.03			8.64	19.0 ± 0.9
						8.69	6.26 ± 0.52
						8.70	11.2 ± 0.4

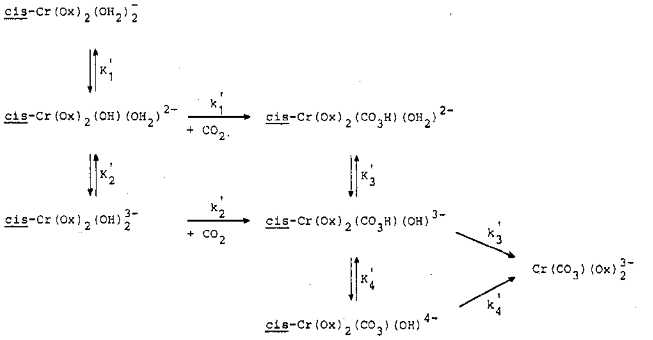
[a] $[CO_2] = 0.01$ M; $I = 0.5$ M, NaCl. k'_{obsd} has the units s^{-1}.

Table IV. Rate Parameters for the Carbon Dioxide Uptake by $Cr(ox)_2(OH_2)_2^-$ [a]

T, °C	k'_1, M^{-1} s^{-1}	pK'_1 [b]	pK'_2 [b]
25	107	6.96	8.97
20	71	7.00	9.01
15	50.5	7.08	9.12
10	34	7.13	9.19

[a] $\Delta H_1^‡ = 12.1 \pm 0.3$ kcal mol^{-1}; $\Delta S_1^‡ = -8.6 \pm 1.2$ cal deg^{-1} mol^{-1}. [b] The errors in pK'_1 and pK'_2 are ca. 0.03 and 0.06, respectively.

Scheme I



These data are interpreted in terms of the reaction sequence in Scheme I.

The pK'_1 and pK'_2 values determined in this study are in reasonable agreement with earlier measurements.[22] Within the range of pH used here, the "aquo" complex ion consists of a pH-dependent mixture of all three species: cis-$Cr(ox)_2(OH_2)_2^-$, cis-$Cr(ox)_2(OH)(OH_2)^{2-}$, and cis-$Cr(ox)_2(OH)_2^{3-}$. Thus, the reactions in Scheme I require that for the relatively rapid reactions described by k'_1 and k'_2[6]

$$-\frac{d}{dt}(\text{total "aquo" complex}) = \{k'_1(Cr(ox)_2(OH)(OH_2)^{2-}) + k'_2(Cr(ox)_2(OH)_2^{3-})\}[CO_2] \qquad (6)$$

which rearranges to give the observed pseudo-first-order rate constant k'_{obsd}:

$$k'_{obsd} = \frac{(k'_1K'_1[H^+] + k'_2K'_1K'_2)[CO_2]}{[H^+]^2 + K'_1[H^+] + K'_1K'_2} \qquad (7)$$

Plots of $([H^+]^2 + K'_1[H^+] + K'_1K'_2)k'_{obsd}/K'_1[CO_2]$ vs. $[H^+]$ yield straight lines with slopes k'_1 and intercepts of $k'_2K'_2$, as shown in Figure 3. The k'_1, K'_1, and K'_2 values at various temperatures are listed in Table IV. As is evident from Figure 3, the intercept at each temperature is negligibly small. This phenomenon is certainly not due to the inactivity of the $Cr(ox)_2(OH)_2^{3-}$ species, but rather to the large uncertainty in k'_{obsd} at higher pH due to the slow concurrent hydrolysis of the oxalate ligands[23] and to the more rapid hydrolysis of CO_2 at high pH.[24] A further contributing factor is the probable similarity between the spectra of cis-$Cr(ox)_2(OH)_2^{3-}$

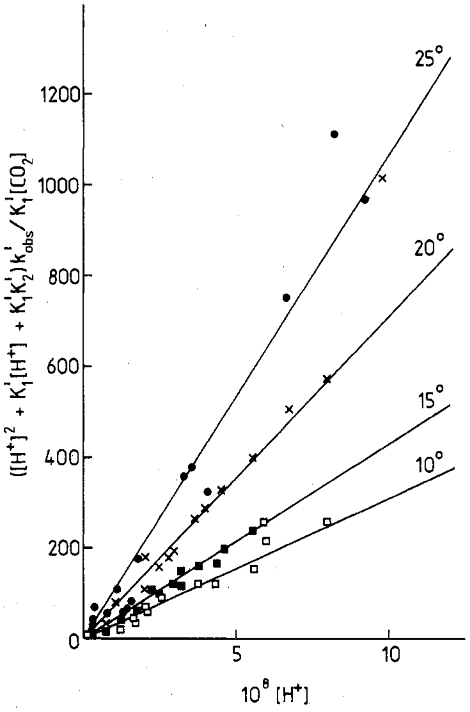


Figure 3. Plots according to the rate expression (7) at various temperatures.

Table V. Rates of CO_2 Uptake by Various Hydroxoaquo Complexes of Cobalt(III) and Chromium(III) at 25 °C, $I = 0.5$ M

Complex ion	k'_1, M^{-1} s^{-1}	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, cal deg^{-1} mol^{-1}	Ref
$Co(NH_3)_5OH^{2+}$	220	15.3 ± 0.9	3.6 ± 3.0	9
$Co(tren)(OH_2)(OH)^{2+}$	44	14.7 ± 0.1	−1.9 ± 0.2	6
cis-$Co(en)_2(OH_2)(OH)^{2+}$	240	15.3 ± 0.9	3.4 ± 3.2	25
cis-$Co(cyclam)(OH_2)(OH)^{2+}$	57	14.8 ± 1.0	0.8 ± 3.5	7
$Cr(NH_3)_5OH^{2+}$	7			26
$Cr(ox)_2(OH_2)(OH)^{2-}$	107	12.1 ± 0.3	−8.6 ± 1.2	This work

Table VI. Rate Constants for the Ring Closure of $Cr(ox)_2(HCO_3)(OH)^{3-}$ at 25 °C, $I = 0.5$ M (NaCl)

pH	10^2k_{obsd}, s^{-1}	pH	10^2k_{obsd}, s^{-1}
7.09	4.28 ± 0.03	7.60	2.10 ± 0.04
7.17	2.10 ± 0.28	7.71	2.21 ± 0.19
7.18	1.27 ± 0.17	7.78	2.28 ± 0.19
7.34	2.70 ± 0.06	7.97	1.48 ± 0.12
7.40	3.41 ± 0.04	8.03	1.56 ± 0.02
7.46	2.85 ± 0.11	8.04	1.67 ± 0.11
7.48	2.76 ± 0.30	9.18	2.70 ± 0.07
7.56	2.02 ± 0.15		

and *cis*-$Cr(ox)_2(CO_3)(OH)^{4-}$.

It is now of interest to compare the rate parameters for CO_2 uptake by the more extensively studied *cis*-aquoammine complexes of cobalt(III)[3] with the results of the present system. These rate parameter data are summarized in Table V. It is apparent that k'_1 for *cis*-$Cr(ox)_2(OH)(OH_2)^{2-}$ is very similar to the corresponding values for the cobalt(III) complexes. This similarity also exists between the activation parameters. The entropy of activation for the bis(oxalato) complex is slightly more negative than the others which emphasizes that little or no disruption of the solvation shell takes place. The rate constant for CO_2 uptake by $Cr(NH_3)_5(OH)^{2+}$ has been estimated to be only 7 M^{-1} s^{-1} as a lower limit from a study[26] of CO_2-catalyzed O exchange with this complex. This value is significantly lower than k'_1 determined for *cis*-$Cr(ox)_2(OH)(OH_2)^{2-}$, which is surprising as one would not expect the magnitude of the charge on the substrate to affect the rate of such a direct associative reaction involving a neutral CO_2 molecule. It is noteworthy that the formation of a stable $Cr(NH_3)_5CO_3^+$ ion was not established[26] and the mechanism of exchange is based on the formation of an unstable carbonato complex intermediate. Recently, Dasgupta and Harris[7] showed that a reasonable correlation exists between log *k* for the CO_2 addition to coordinated hydroxide and the pK_a of the conjugate aquo acid. The rate of CO_2 uptake by *cis*-$Cr(ox)_2(OH)(OH_2)^{2-}$ satisfactorily fits into that correlation (see Figure 3 in ref 7). However, the log *k* value for $Cr(NH_3)_5(OH)^{2+}$ was found to be too small to reasonably fit the linear correlation.

The ring closure rate data for *cis*-$Cr(ox)_2(HCO_3)(OH)^{3-}$ are presented in Table VI. These rate constants correspond to the comparatively slow release of oxalate at high pH. Therefore, these results cannot be discussed in detail. Nevertheless, it is interesting to note that the rate of ring closure is similar to that observed for cobalt(III)–ammine monodentate carbonato complexes,[7] i.e., in the range 10^{-2} s^{-1}. This alone suggests that ring closure of the carbonatoaquo complexes of chromium(III) also follow a S_N2(internal) mechanism, as proposed earlier.[7] However, an unequivocal assignment of the mechanism for ring closure necessitates additional studies of other chromium(III) activation parameters.

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Registry No. $Cr(CO_3)(ox)_2^{3-}$, 65915-84-6; $K_3[Cr(CO_3)(ox)_2]$, 65890-26-8; H^+, 12408-02-5; *cis*-$Cr(ox)_2(OH_2)_2^-$, 15489-30-2; K_2CO_3, 584-08-7.

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