Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. 11. Carbon Dioxide Uptake and Intramolecular Carbonato Ligand Chelation in Aqueous Solution of *cis*- and *trans*-Diaquo(1,4,8,11-tetraazacyclotetradecane)-cobalt(III) Cations[1]

T. P. Dasgupta and G. M. Harris* [2]

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received September 20, 1976*

Abstract: The rapid reactions of the title compounds with CO_2 were studied by stopped-flow spectrometry in the range $6 < pH < 9$ and $15° < t < 25°$ at an ionic strength of 0.5 M ($NaClO_4$). Under these conditions, the major reactant species are *cis*- and *trans*-$Co(cyclam)(OH)(OH_2)^{2+}$ and $Co(cyclam)(OH)_2{}^+$, all of which take up CO_2 at similar rates to form *cis*- and *trans*-$Co(cyclam)(OH_2)(HCO_3)^{2+}$ and $Co(cyclam)(OH)(HCO_3)^+$. Subsequently, relatively slow ring-closure of the cis products to form the carbonato chelate is observed, and rate data for the process are presented. The trans carbonato species, however, are completely stereoretentive, so no chelation is possible, nor is any evidence obtained for the uptake of additional CO_2 to form identifiable trans bis(carbonato) complexes. The CO_2 uptake rate constants of the various hydroxo metal complexes so far studied show a linear correlation with the acidities of their aquo congeners of the form $\log k = (1.11 \pm 0.34) + (0.163 \pm 0.050)pK_a$. This relation predicts a value close to that observed for the corresponding reaction of free hydroxide ion, but is high by several orders of magnitude for H_2O and low by an even larger factor for carbonic anhydrase. Comparisons are also made among the results of several intramolecular ligand chelation studies, including those of other types of oxyanions, and possible mechanisms are discussed.

We have reported in our earlier paper[3] detailed kinetic results concerning the carbon dioxide uptake by the complex ion $Co(tren)(OH_2)_2{}^{3+}$ (where tren ≡ 2,2′,2″-triaminotriethylamine) and the subsequent slower carbonato ligand chelation reaction. In this case, only cis-diaquo complex is possible because of the steric requirements of the tren ligand. We were thus able to avoid the complication of possible cis/trans isomerization in both the uptake and ring-closure processes. We have now studied the CO_2 uptake reaction with another type of diaquo cobalt(III) complex where the quadridentate ligand attached to the metal center is 1,4,8,11-tetraazacyclotetradecane (cyclam). Cyclam is an interesting ligand in various ways. It is the only macrocyclic ligand which so far as is known forms both cis and trans arrangements with the same unidentate ligands.[4,5] Both cis and trans Co(III) cyclam-diacido complexes undergo stereoretentive substitution,[5] although the cis products undergo subsequent isomerization to geometrically stable trans analogues. However, the rate of cis → trans interconversion of the diaquo complex is slow enough[6] that both CO_2 uptake and carbonato ligand chelation of the cis congener can be investigated without interference from the isomerization process. In the case of the stereochemically inert trans reactant, the carbonato product of CO_2 uptake does not undergo chelation, but the formation of trans bis(carbonato) complex species is a possibility which has been examined in this study.

Experimental Section

Preparation of Compounds. All chemicals were of reagent grade and deionized degassed water was used in preparing all solutions. 1,4,8,11-Tetraazacyclotetradecane (cyclam) was prepared starting from commercially available 1,3-bis(2′-aminoethylamino)propane and 1,3-dibromopropane using the method of Bosnich et al.[7] Sodium triscarbonatocobaltate(III) trihydrate was prepared by the method of Bauer and Drinkard.[8] *cis*-Carbonato(1,4,8,11-tetraazacyclotetradecane)cobalt(III) chloride was prepared by a method similar to that of Poon and Tobe.[4] Four grams of solid cyclam·3.5HCl (prepared by adding cold concentrated HCl to a methanolic solution of cyclam in an ice bath) was dissolved in 25 mL of water and 5 g of freshly prepared sodium triscarbonatocobaltate(III) trihydrate was gradually added with stirring. The resultant solution was heated on a steam bath for 15 min. The red solution was allowed to cool and was filtered. Ethanol and acetone were then added in excess to the red filtrate which was stored in the refrigerator for 12 h. The crude precipitated product was filtered off, washed with acetone, and recrystallized several times by addition of acetone to a cold methanolic solution of the complex. The purity of the compound was checked by microanalysis.[9] Calcd for $[Co(cyclam)CO_3]Cl$: C, 37.27; H, 6.77; N, 15.80. Found: C, 37.02; H, 6.65; N, 15.90.

cis- and *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) chloride were prepared as described previously.[4,7] The purity of each was checked by comparing the visible spectrum with that reported in the literature.[10]

cis- and *trans*-diaquo(1,4,8,11-tetraazacyclotetradecane)cobalt(III) complex ions were usually generated in solution by basic hydrolysis of the dichloro complex and then acidifying the resultant dihydroxo product. A measured quantity of dichloro complex is shaken with anion exchange resin (Amberlite 400) in the hydroxide form suspended in a small volume of water. The slurry is poured into an ice-water-jacketed column of the same resin. The effluent and washings are made acidic (pH 1) by adding 4 M $HClO_4$ and diluting to the necessary volume.

Absorption Spectra. The visible absorption spectra of the various complexes of significance to this research are presented in Figures 1 and 2. Generally, these were obtained at room temperature either with a Cary Model 15 or Cary Model 118C instrument, using matched 2-cm quartz cells. The spectra of the *cis*- and *trans*-$Co(cyclam)(H_2O)_2{}^{3+}$ species, run in acidic solution (pH 1.5), were found to be identical with those of authentic samples prepared independently by the published procedure.[4] The spectra of the dihydroxy congeners were obtained at pH 9, and that of *trans*-$Co(cyclam)(OH)(OH_2)^{2+}$ at pH 5.5, roughly half-way betweeen the two widely separated p*K* values.[11] The spectrum of *cis*-$Co(cyclam)(OH)(HCO_3)^+$ was obtained at 10 °C on the Cary 118C instrument using the fast scanning device after rapid manual mixing of CO_2 solution at pH 3 containing diaquo compound with buffer solution at pH 7.5. The spectra of the trans hydroxobicarbonato and trans hydroxocarbonato species were determined in a similar manner to that just described, using buffers at pH 6 and pH 9, respectively.[12] The possibility exists that these trans carbonato species are in fact bis(carbonato) complexes. To test for this possibility a large excess of CO_2 (and carbonate) in the uptake

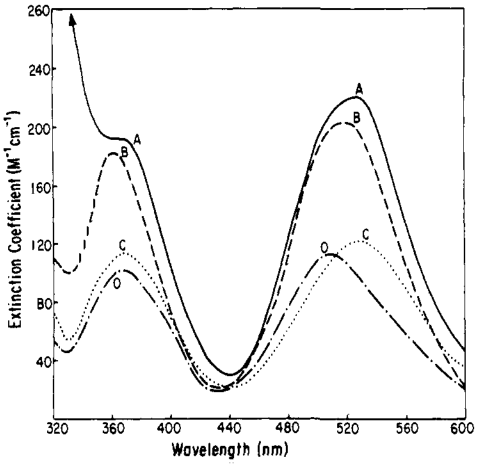


Figure 1. Spectra of *cis*-(cyclam)Co(III) complexes: (A) *cis*-[Co(cyclam)(OH)(HCO_3)]$^+$ (extinction coefficient at 330 nm is ~600); (B) *cis*-[Co(cyclam)CO_3]$^+$; (C) *cis*-[Co(cyclam)$(OH)_2$]$^+$ (diaquo complex at pH 9); (D) *cis*-[Co(cyclam)$(OH_2)_2$]$^{3+}$ (diaquo complex at pH 1.5).

reaction was ensured by the following procedure. A filtered 10% lithium hydroxide solution was added dropwise to 10 mL of 0.05 M *trans*-Co(cyclam)$(OH)_2{}^+$ (prepared following the procedure mentioned above) until the pH of 9-9.5 was reached. CO_2 was then bubbled slowly through the solution kept in an ice bath, the pH being maintained within the specified range by occasional dropwise addition of LiOH solution, until a constant spectrum was obtained.[13] This spectrum could not be distinguished from that obtained earlier with limited CO_2 excess and ascribed to the species *trans*-Co(cyclam)(OH)(CO_3). However, to confirm this identification, the "constant spectrum" solution was passed through a cold-water-jacketed ion-exchange column (Bio-Rex chromatography column, i.d. 0.9 cm, length, 25 cm) filled with anion exchange resin (Bio-Rad AG1X8, $HCO_3{}^-$ form). None of the complex was adsorbed on the column, all being easily eluted by water. That the displacement of $HCO_3{}^-$ by a large anion of the type Co(cyclam)$(CO_3)_2{}^-$ should readily occur is suggested by the experimental observation that the large cation Co(cyclam)$(OH)_2{}^+$ easily displaces Na^+ from a cation exchange column. We can therefore conclude that the carbonato complex ion eluate is uncharged. The spectrum of the solution after elution was found to be the same as that observed before ion-exchange chromatography, indicating that no reaction occurs on the column. All the evidence thus suggests that a bis(carbonato) complex is not a stable entity under our conditions notwithstanding the presence of excess of CO_2 and other "free" carbonate species. We therefore conclude that the uncharged eluate is indeed *trans*-Co(cyclam)(OH)(CO_3), as is the product of identical spectrum obtained initially in limited CO_2 excess.

Kinetics. Carbon dioxide uptake by the *cis*- and *trans*-diaquocobalt(III) complexes was investigated by the "acidification technique" using a Durrum stopped-flow kinetics spectrometer as previously described,[3] though some modifications were necessary for the cis cogener. The ionic strength of the reacting solutions was maintained at 0.5 M ($NaClO_4$). For pH's less than 8.5, 2,6-lutidine/$HClO_4$ mixture was used as buffer, while in the higher pH range, boric acid/borax was employed. All pH measurements were made either with a Beckman Research Model or a Radiometer Model 26 meter.

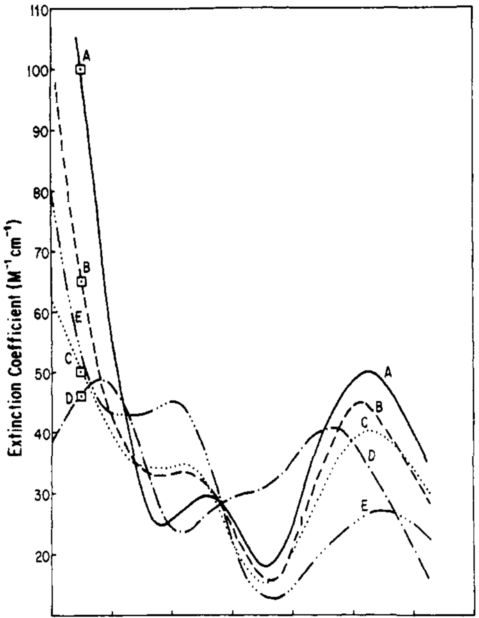


Figure 2. Spectra of *trans*-(cyclam)Co(III) complexes: (A) *trans*-[Co(cyclam)(OH)(CO_3)]; (B) *trans*-[Co(cyclam)(OH)(HCO_3)]$^+$; (C) *trans*-[Co(cyclam)(OH)(OH_2)]$^{2+}$ (diaquo complex at pH 5.5); (D) *trans*-[Co(cyclam)$(OH)_2$]$^+$ (diaquo complex at pH 9); (E) *trans*-[Co(cyclam)$(OH_2)_2$]$^{3+}$ (diaquo complex at pH 1.5).

Table I. Observed Rate Constants for the Carbon Dioxide Uptake Reactions of Diaquo(cyclam)cobalt(III) Complex Ions

15 °C		20 °C		25 °C	
pH	$k_{obsd}/[CO_2]$ ($M^{-1}s^{-1}$)	pH	$k_{obsd}/[CO_2]$ ($M^{-1}s^{-1}$)	pH	$k_{obsd}/[CO_2]$ ($M^{-1}s^{-1}$)
A. Trans Complex (I = 0.5 M, $NaClO_4$; $[CO_2]$ = 0.01 M)					
5.85	6.8	5.92	16.6	5.95	39.1
6.22	7.2	6.10	16.8	6.35	41.4
6.52	7.7	6.45	18.0	6.85	47.5
6.80	8.4	6.82	20.0	6.90	48.3
7.25	10.0	6.98	21.2	7.15	52.8
7.56	11.0	7.20	22.9	7.45	58.3
7.85	11.8	7.55	25.6	7.65	61.6
8.22	12.4	7.65	26.3	7.95	65.2
8.55	12.7	7.95	27.9	8.45	68.4
9.02	12.9	8.30	29.0	8.65	69.0
		8.62	29.5	9.05	69.7
		8.98	29.8		
k_{1t} ($M^{-1}s^{-1}$)	6.57 ± 0.01		15.9 ± 0.1		37.3 ± 0.1
k_{2t} ($M^{-1}s^{-1}$)	13.0 ± 0.1		29.7 ± 0.3		70.1 ± 0.2
B. Cis Complex (I = 0.5 M, $NaClO_4$; $[CO_2]$ = 0.005 M)					
6.98	28	7.05	46	6.96	68
7.16	32	7.08	48	7.05	76
7.44	28	7.10	42	7.09	68
7.52	42	7.18	48	7.23	80
7.56	32	7.25	42	7.24	70
7.72	30	7.37	52	7.31	80
7.74	50	7.76	56	7.55	114
8.21	56	7.91	92	7.71	92
8.45	84	8.39	110	7.76	122
		8.50	106	7.92	100
				8.22	142
k_{1c} ($M^{-1}s^{-1}$)	23 ± 3		35 ± 3		57 ± 4
k_{2c} ($M^{-1}s^{-1}$)	78 ± 13		128 ± 16		196 ± 24

For the cis complex, a "pH-jump" technique was devised so as to avoid possible cis → trans isomerization complications. One reservoir syringe of the stopped-flow device was filled with the appropriate buffer solution,[14] and the second syringe with a solution of diaquo complex and carbon dioxide at a pH of approximately 3. The latter solution was prepared by dissolving calculated amounts of $NaHCO_3$ and $NaClO_4$ in water, adjusting to pH 3 with $HClO_4$, and adding the requisite amount of stock solution of cis diaquo complex, also at a pH of 3. The spectra of such solutions correspond to that of the diaquo complex and show no appreciable change during a period of 2 or 3 h.[15] The concentrations of cis-cyclam complex and CO_2(M) were 10^{-3} and 5×10^{-3}, respectively. At the pH's of the experiments, the rate of CO_2 uptake is about 100 times as great as cis → trans isomerization of the diaquo reactant, so no interference occurs between these processes. The subsequent carbonato chelation of the hydroxobicarbonato intermediate is only about five times more rapid than the isomerization of the diaquo,[6] but the final product spectra were always identical with that of the separately prepared cis chelate, $Co(cyclam)CO_3^+$. Possible competing cis → trans isomerization of the intermediate species is therefore ruled out. Rate data for the CO_2 uptake and chelation reactions were obtained at 330 nm, with some runs at 520 nm, the wavelength choices being made on the basis of the known spectra as shown in Figure 1. Because of the large rate difference between the two reactions just specified, complete separation of the kinetics data is possible in a manner analagous to that utilized for the tren complex.[3]

In the case of the trans diaquo species, no isomerization complications ensue, so the standard "acidification technique" is applicable.[16] Usually, the complex solution was obtained directly as the effluent from the ion exchange column as described in the preparative procedure. In some experiments, the trans diaquo complex was generated by hydrolyzing the requisite amount of trans dichloro congener with 1 N NaOH and then diluting the resultant solution by the appropriate buffer solution. The same kinetic results were obtained by both procedures. In a typical experiment the concentration of complex ion was 10^{-3} M and that of CO_2 10^{-2} M. The reaction was monitored at 370 nm where the absorbance difference between reactant aquo and product carbonato species is reasonably large at all pH values utilized (see Figure 2). The pseudo-first-order experimental rate constants, k_{obsd}, were determined in the usual graphical manner from semilogarithmic plots of $(A_\infty - A_t)$ vs. time.

Results and Discussion

The carbon dioxide uptake study was performed in the range $15° < t < 25°$ and $5.9 < pH < 9.0$. The data are given in Table I, and have been treated in a manner analogous to the method employed in the case of the "tren" complex.[3] The assumed mechanism is:

$$\begin{tikzcd}
Co(cyclam)(OH_2)_2^{3+} \arrow[d, shift right, "K_1"'] & & \\
Co(cyclam)(OH)(OH_2)^{2+} \arrow[u, shift right] \arrow[r, "k_1", "CO_2"'] \arrow[d, shift right, "K_2"'] & Co(cyclam)(OH_2)(HCO_3)^{2+} \arrow[d, shift right, "K_3"'] & (1) \\
Co(cyclam)(OH)_2^{+} \arrow[u, shift right] \arrow[r, "k_2", "CO_2"'] & Co(cyclam)(OH)(HCO_3)^{+} \arrow[u, shift right] \arrow[d, shift right, "K_4"'] & (2) \\
& Co(cyclam)(OH)(CO_3) \arrow[u, shift right] &
\end{tikzcd}$$

As already discussed above, the diaquo form is justifiably taken to be inactive to CO_2 addition. In any case, since pK_1 is much smaller than the minimum pH of the experiments for both cis and trans species,[11] the mechanism leads directly to the rate equation previously derived,[3] viz.:

$$k_{\text{obsd}}\left[\frac{[H^+] + K_2}{[CO_2]}\right] = k_1[H^+] + k_2K_2 \tag{3}$$

Plots of the left-hand side of eq 3 vs. $[H^+]$ (assuming constant K_2 values within the temperature range given[17]) yield straight lines of slope k_1 and intercept k_2K_2. Linear regression analysis enables evaluation of the k_1 and k_2 values, which are recorded with their standard deviations at the foot of Tables IA and IB for trans and cis complexes, respectively. The conventionally evaluated temperature variation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, are presented in Table III, where comparisons may be drawn with several other systems for which data are at hand. One notes that all the rate constants at 25 °C, whether for uptake by mono- or dihydroxy species, lie within the range of about 40 to 200 $M^{-1}\ s^{-1}$, with a factor of about 4 between the various cis-$(OH)(OH_2)$ and cis-$(OH)_2$ species and the expected statistical factor of 2 for the two trans (cyclam) species. Also, for the pentaammine complex and all the cis complexes, the temperature parameters are identical within experimental error, with $\Delta H^\ddagger = 15$ kcal/mol and $\Delta S^\ddagger \sim 0$. For these CO_2 uptake reactions, it appears that the gain in entropy due to solvent shell disordering is cancelled out by the loss in entropy accompanying formation of a highly structured transition state. The latter may be visualized by the figure shown below where it is seen that hydrogen bonding plays an important role.[19] However, the CO_2 addition reactions of the trans (cyclam) species (reactants 4 and 5) exhibit very different activation parameters, both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ being very much higher than for the cis congeners. The intimate mechanism of these reactions must be considerably different from that just proposed, with the large positive $\Delta S^\ddagger$ value suggesting a rather disorganized transition state. This may result from the impossibility of achieving the highly structured double H-bonded transition state suggested above, due to the absence of the cis aquo (or hydroxo) grouping. This factor could also account for at least part of the ~14 kcal/mol increase in $\Delta H^\ddagger$ for the trans complexes as compared to their cis congeners.

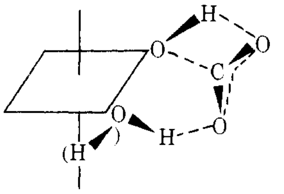


Table II. Observed Rate Constants for the Ring-Closure Reaction of *cis*-Aquocarbonato(cyclam)cobalt(III) Complex Ion ($I = 0.5$ M, $NaClO_4$)

15 °C		20 °C		25 °C	
pH	10^2k_{obsd} (s^{-1})	pH	10^2k_{obsd} (s^{-1})	pH	10^2k_{obsd} (s^{-1})
6.98	1.0	7.05	1.4	7.31	2.5
7.16	1.0	7.15	1.4	7.34	2.4
7.22	1.0	7.19	1.4	7.43	2.1
7.29	1.0	7.24	1.4	7.75	2.2
7.38	1.0	7.33	1.5	8.17	1.9
7.53	0.9	7.45	1.4	8.22	2.4
7.76	1.1	7.78	1.3	8.22	2.5
7.92	1.0	8.15	1.3	8.55	1.5
8.21	0.8	8.45	1.0	8.85	1.2
8.50	0.6	8.80	0.7		
10^2k_3 (s^{-1})[a]	1.0 ± 0.1		1.4 ± 0.1		2.3 ± 0.2
$\Delta H^\ddagger = 13.6 \pm 1.7$ (kcal/mol)			$\Delta S^\ddagger = -20.7 \pm 5.8$ (cal deg^{-1} mol^{-1})		

[a] Average of k_{obsd} values excluding two at highest pH's (see Discussion).

It has been noted above that the CO_2 uptake rates by the various aquocobalt(III) complexes are only moderately sensitive to the nature of the "nonparticipating" ligands. However, utilizing the data for the enlarged group of hydroxo complex ion reactants which we now have available, reasonable adherence to the previously suggested[20] correlation of log k for CO_2 addition to ligand hydroxide vs. pK_a of the conjugate aquo acid is noted, as illustrated in Figure 3. The linear least-squares curve[27] has an intercept of 1.11 ± 0.34 and a slope of 0.163 ± 0.050. The most notable deviants from the plot are the hydroxopentaamminerhodium(III) and -iridium(III) complexes (no. 3 and 1, respectively). For these, the central metal ions, unlike those in the other examples given, are beyond the first-row transition elements, so some kinetic differences are to be expected. The very long extrapolation of the curve to the pK_a value of H_2O (15.7) predicts a satisfactory value for the magnitude of the rate constant for the CO_2/OH^- reaction (log $k_{\text{calcd}} = 3.7 \pm 0.4$, log $k_{\text{obsd}} = 3.9$). Extrapolation in the other direction to the pK_a value of H_3O^+ (−1.7) predicts a k value for the CO_2/H_2O reaction about four orders of magnitude too

Table III. Rates of Carbon Dioxide Uptake by Various Polyamineaquocobalt(III) Complexes (temp = 25 °C, I = 0.5 M)

Complex ion	k ($M^{-1}\,s^{-1}$)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal deg^{-1} mol^{-1})	Ref
(1) $Co(NH_3)_5OH^{2+}$	220	15.3 ± 0.9	3.6 ± 3.0	16
(2) $Co(tren)(OH_2)(OH)^{2+}$	44[a]	14.7 ± 0.1	−1.9 ± 0.2	3
(3) *cis*-$Co(en)_2(OH_2)(OH)^{2+}$	240	15.3 ± 0.9	3.4 ± 3.2	18
(4) *trans*-$Co(cyclam)(OH_2)(OH)^{2+}$	37	29.0 ± 0.1	46.2 ± 0.4	This work
(5) *trans*-$Co(cyclam)(OH)_2^+$	70	28.3 ± 0.6	44.6 ± 1.9	
(6) *cis*-$Co(cyclam)(OH_2)(OH)^{2+}$	57	14.8 ± 1.0	0.8 ± 3.5	
(7) *cis*-$Co(cyclam)(OH)_2^+$	196	15.2 ± 0.5	3.0 ± 1.9	

[a] For the $Co(tren)(OH)_2^+$ species, a reliable value of 170 $M^{-1}\,s^{-1}$ at 25 °C was observed (ref 3) but the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were subject to large errors and are not quoted.

large ($\log k_{calcd} = 0.8 \pm 0.4$, $\log k_{obsd} = -3.2$). However, in this instance there must be an unusual reaction mechanism, since it is difficult to visualize a simple transition-state geometry involving such a highly structured reactant as liquid water. The naturally occurring metal complex, carbonic anhydrase, in which the site of CO_2 hydrolysis is believed to be the Zn^{II}-OH grouping,[28] has a pK_a between 7 and 8, but the second-order rate constant for CO_2 "turnover" has a magnitude[16] of about 4×10^7 $M^{-1}\,s^{-1}$ at 25 °C, far above the prediction of Figure 3. Here deviation from the pattern of the simple complex ions is again to be expected, in view of the known strong binding of the CO_2 molecule at the active site, possibly facilitated by the presence of the adjacent conical cavity in the enzyme.[28]

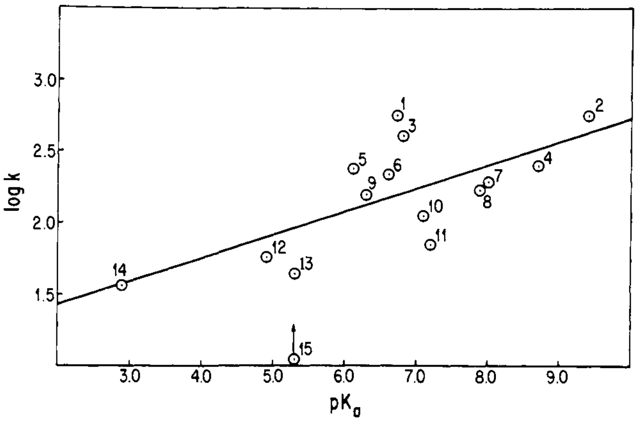


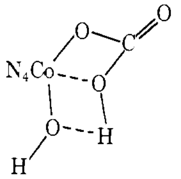
Figure 3. Plot of log of rate constant for CO_2 reaction with various hydroxo metal complexes vs. pK_a of corresponding aquo form of complex: (1) $[Ir(NH_3)_5OH]^{2+}$ (ref 21), (2) [Cu(glygly)OH] (ref 22), (3) $[Rh(NH_3)_5OH]^{2+}$ (ref 21), (4) $[Zn(CR)OH]^+$ (ref 23), (5) *cis*-$[Co(en)_2(OH)(OH_2)]^{2+}$ (ref 18), (6) $[Co(NH_3)_5OH]^{2+}$ (ref 16), (7) *cis*-$[Co(cyclam)(OH)_2]^+$ (this work), (8) $[Co(tren)(OH)_2]^+$ (ref 3), (9) $\alpha\beta$-(*S*)-Co(tetraethylenepentamine)OH^{2+} (ref 24), (10) *cis*-$[Cr(C_2O_4)_2(OH)(OH_2)]^{2-}$ (ref 25), (11) *trans*-$[Co(cyclam)(OH)_2]^+$ (this work), (12) *cis*-$[Co(cyclam)(OH)(OH_2)]^{2+}$ (this work), (13) $[Co(tren)(OH)(OH_2)]^{2+}$ (ref 3), (14) *trans*-$[Co(cyclam)(OH)(OH_2)]^{2+}$ (this work), (15) $[Cr(NH_3)_5OH]^{2+}$ (ref 26).

The ring-closure rate data for the cis cyclam system are presented in Table II. One notes that the observed rate constants are invariant at each of the three temperatures from the lowest pH values (~7) up to about pH 8, when a fall-off begins to be observed. Runs at higher pH's were not attempted, but by analogy to the earlier work,[3] ring-closure of the species *cis*-$Co(cyclam)(OH)(CO_3)$ is expected to be very slow, thus accounting for the steep decline of k_{obsd} beyond pH 8. Also, the species $Co(cyclam)(OH_2)(HCO_3)^{2+}$ formed in reaction 1 is quite acidic and immediately deprotonates according to the equilibrium described by K_3. The ring-closure rate constants, k_3, therefore refer only to the reaction:

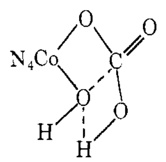
$$cis\text{-}Co(cyclam)(OH)(HCO_3)^+ \rightarrow cis\text{-}Co(cyclam)CO_3^+ + H_2O \quad (4)$$

These constants have been determined by averaging all the values obtained at each temperature except those at the highest pH's, beyond the point at which the fall-off in rate commences. These values are recorded in Table II, together with the magnitudes of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as evaluated in the usual way.

This new carbonato chelation rate data, together with similar results for a number of other systems, are summarized in Table IV. It is noted that for all pairs of compounds which differ only by one proton, the ring-closure rate constant is considerably slower for the deprotonated type than for the parent species. These differences range from fairly large values of between 500 and 700 for the (1), (2) and (4), (5) pairs, respectively, to a moderate value of 40 for the (6), (7) pair, down to low values of about 4 for the (8), (9) and (11), (12) pairs, respectively. The temperature parameters suggest similar mechanisms for all three hydroxobicarbonato ring-closures (reactants 1, 3, and 4). Furthermore, the rates of these processes are between 25 and 50 times greater than expected for a simple dissociative mechanism in which chelation occurs within a five-coordinate intermediate subsequent to loss of a cis aquo ligand. This expectation is based on our earlier conception[3] of a bicyclic transition state for ring closure of the form:



This assumes Co–O bond-making by analogy to the known first-step Co–O bond-breaking process for acid hydrolysis of tetraammine carbonato chelate,[36] where, however, an additional proton is present in the transition state. An alternative view, taking into account the now well-known nucleophilicity of ligand OH for reaction with carbon on an adjacent ligand,[37] suggests C–O bond-making according to the following transition state:



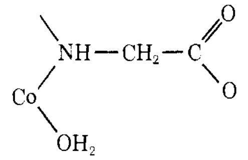
In the first proposal it is seen that the H-bonding of the bicarbonato proton to the hydroxo oxygen produces an incipient aquo ligand, which we assume would have a dissociation rate similar to that of the aquo ligand in a $CoN_4(OH)(OH_2)^{2+}$ ion, such as suggested by the aquo exchange rate included in Table

Table IV. Rates of Oxyanion Ligand Chelation of Various Aquocarboxylatocobalt(III) Complex Ions at 25 °C

Complex	10^3k (s^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal deg^{-1} mol^{-1})	Ref
(1) Co(tren)(OH)(HCO_3)$^+$	50	13	−23	3
(2) Co(tren)(OH)(CO_3)	~0.1	—	—	29[a]
(3) *cis*-Co(cyclam)(OH)(HCO_3)$^+$	23	14	−22	This work
(4) *cis*-Co(en)$_2$(OH)(HCO_3)$^+$	44	16	−12	18
(5) *cis*-Co(en)$_2$(OH)(CO_3)	0.06	28	17	30
(6) Co(EDTA)(OH_2)$^-$	1.7	25	12	31[b,c]
(7) Co(EDTA)(OH)$^{2-}$	0.04	19	−16	31[b,c]
(8) Co(PDTA)(OH_2)$^-$	2.0	24	8	32[b,d]
(9) Co(PDTA)(OH)$^{2-}$	0.25	15	−26	32[b,d]
(10) Co(CyDTA)(OH_2)$^-$	0.7	19	−10	33[e]
(11) Co(HyDTA)(OH_2)$^-$	0.02	28	13	34[f]
(12) Co(HyDTA)(OH)$^{2-}$	0.005	22	−9	34[f]
(13) *cis*-Co(en)$_2$(OH)(OH_2)$^{2+}$	0.9	—	—	35[g,h]
(14) *cis*-Co(en)$_2$(OH)$_2$$^+$	0.03	27	13	35[g]

[a] Data at 20 °C only available. [b] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values recalculated using the original rate constant data. [c] EDTA = ethylenediamine-*N,N,N',N'*-tetraacetate. [d] PDTA = propylenediamine-*N,N,N',N'*-tetraacetate. [e] CyDTA = *trans*-1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetate. [f] HyDTA = *N*-(2-hydroxyethyl)-*N,N',N'*-triacetate. [g] Oxygen exchange rate data. [h] Data given at 25 °C only.

IV (reactant 13).[38] It is noted, however, that, while the rate constants for acid-catalyzed ring-opening of Co(tren)CO_3^+ and Co(cyclam)CO_3^+ differ[39] by a factor of 1500 at 25 °C, the rates of ring-closure of the species Co(tren)(OH)(HCO_3)$^+$ and *cis*-Co(cylam)(OH)(HCO_3)$^+$ differ by a factor of only 2. It thus seems more than likely that the intimate mechanisms of the two types of reaction are widely different, so that our second alternative proposal for the chelation mechanism, involving C–O bond-making, is to be preferred. In either case, carbonato chelation may be classed as having an S_N2 (internal) mechanism, such as has been discussed previously in connection with the chelation rates of cobalt(III) aquodiaminepolycarboxylato complexes.[31,33] The data for some compounds of this type are given in Table IV (reactants 6, 8, and 10), all of which undergo ring-closure by the free carboxylate arm at rates much slower than those of the carbonato species just discussed. The process for the former involves the grouping



so that the chance of getting a hydrogen-bonded juxtaposition of the aquo and oxyanion groupings favorable to ring-closure is bound to be much smaller for the carboxylato than for the carbonato species. Dissociation of the aquo ligand could thus very well be the rate-determining process for the aminepolycarboxylates, a view also supported by the $\Delta S^{\ddagger}$ values but contrary to the earlier opinions.[31,33] The entropies of activation are large and negative for compounds 1, 3, and 4, as expected for the necessarily highly structured transition state for S_N2 (internal) attack. By contrast, the $\Delta S^{\ddagger}$ values for the much more slowly reacting and very similar complexes 6 and 8 are substantially positive, suggesting a rather unstructured transition state as would be expected if ring-closure simply involves a competition between the "free arm" and solvent water for the vacant aquo ligand site *after* departure of the latter to form the five-coordinate intermediate. Reactant 10, with a large negative $\Delta S^{\ddagger}$, does not fit into this pattern but is conceivably subject to specific stereochemical requirements because of the cyclic diamine moiety which may force it into the S_N2 (internal) mode of reaction. Reactant 11 does fit the pattern, though ring-closure here is a very slow process, probably because the "free arm" is the hydroxyethyl grouping which one would expect to be a much less effective competitor for the vacated aquo site than the negatively charged carboxylato entities of the related species.

For the deprotonated species 2 and 5, one must conclude that an entirely different mechanism is operative from that of their protonated parent compounds 1 and 4, since the latter undergo ring-closure hundreds of times more rapidly than the former. It is noted that the rate constant and temperature parameters for hydroxo group dissociation from the complex ion Co(en)$_2$(OH)$_2$$^+$ (as measured by oxygen exchange—see data for reactant 14 in Table IV) are almost identical to the ring-closure rate data for reactant 5. It seem logical to conclude, therefore, that this latter type of chelation is limited by the departure rate of hydroxo ligand, making the reasonable assumption that the complex ions Co(en)$_2$(OH)$_2$$^{2+}$ and Co(en)$_2$(OH)(CO_3) have similar rates of hydroxo ligand dissociation. By contrast, the deprotonated polycarboxylato complexes 7, 9, and 12, while having rather slow rates of ring-closure, have quite different temperature parameters from the simpler reactants 2 and 5. The large negative $\Delta S^{\ddagger}$ values for 7, 9, and 12 suggest a highly structured transition state, perhaps of the bicyclic type suggested above for reactants 1, 2, and 4 (which also exhibit large negative $\Delta S^{\ddagger}$ values). Thus, the S_N2 (internal) mechanism of chelation may also be operative for reactants 7, 9, and 12. In summary, then, we are proposing two types of ring-closure mechanism for oxyanion ligation—one in which internal nucleophilic attack is the rate-determining process, and one in which dissociation of the cis aquo or hydroxo ligand is rate limiting. The best criterion as to which of these predominates for a given type of complex appears to be the negativity or positivity of the entropy of activation.

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(11) The pK_1 and pK_2 values for the trans-diaquo complex are, at 25 °C and $I = 0.5$ M ($NaClO_4$), 2.9 ± 0.1 and 7.2 ± 0.1, respectively, while for the cis congeners, the corresponding values are 4.9 ± 0.2 and 8.0 ± 0.2 (see ref 6). The spectrum for the *cis*-Co(cyclam)$(OH_2)(OH)^{2+}$ species was not recorded since it differs only slightly from the average of its diaquo and dihydroxy analogues.

(12) For the trans species, there is no need for the rapid mixing and scanning, nor for cooling below room temperature, since there is no isomerization and ring closure does not occur with these complexes.

(13) The same spectral result was obtained on long standing in excess of 0.5 M $NaHCO_3$-Na_2CO_3 buffer, but the subsequent ion-exchange experiment could not be carried out with this solution because of the excess of carbonate.

(14) To avoid any appreciable change in pH of the buffer solution, high buffer concentrations (0.2–0.3 M) were used.

(15) This is consistent with our earlier findings that $Co(NH_3)_5H_2O^{3+}$ (ref 16) and Co(tren)$(H_2O)_2^{3+}$ (ref 3) do not react with CO_2, and that the cis → trans isomerization of the acidified solution of Co(cyclam)$(H_2O)_2^{3+}$ complex is very slow (ref 6).

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(38) The exchange rate constant applies, of course, only to the species *cis*-Co(en)$_2$(OH)$(OH_2)^{2+}$, but this should give a reasonable order-of-magnitude estimate for the unknown similar rate constants for the similar tetramine species 1, 3, and 4.

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Photochemistry of Coordination Compounds. 15. *trans*- and *cis*-[Co(en)$_2$(NH$_3$)Cl](NO$_3$)$_2$

Robert A. Pribush, Robin E. Wright, and Arthur W. Adamson*[1]

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007.

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Abstract: The ligand field photolysis (488 nm) of *trans*- and *cis*-[Co(en)$_2$(NH$_3$)Cl](NO$_3$)$_2$ in acidic solution is reported. Quantum yields (all × 10^4) for ammonia aquation (14.8, 2.06, 50.7) and chloride aquation (2.96, 3.10, 17.1) for *trans*-Co(en)$_2$(NH$_3$)Cl^{2+}, *cis*-Co(en)$_2$(NH$_3$)Cl^{2+}, and Co(NH$_3$)$_5$Cl^{2+}, respectively, support a previous suggestion that photolysis rules similar to those for Cr(III) ammines are operative for Co(III) ammines as well. Isomer analysis shows that photoaquation of *trans*-Co(en)$_2$(NH$_3$)Cl^{2+} occurs with essentially complete stereoretention. The principal photoaquation paths for *cis*-Co- (en)$_2$(NH$_3$)Cl^{2+} are more complicated, yielding mainly *cis*-Co(en)$_2$(NH$_3$)(H$_2$O)$^{3+}$ as the chloride photoaquation product but mainly *trans*-Co(en)$_2$(H$_2$O)Cl^{2+} as the ammonia photoaquation product. These results may be accounted for by the same photolysis rules, with the added mechanistic assumption that if one end of an ethylenediamine is labilized it may undergo an edge displacement to detach an adjacent monodentate ligand.

The photochemistry of Co(III) ammines has, until recently, been primarily that following irradiation in the wavelength region of the first charge transfer (CT) band; such irradiation leads to photochemistry dominated by redox decomposition.[2,3] Photochemistry in the wavelength region of the first (and, if uncomplicated by CT characteristics, the second) ligand field band was sparse until the advent of high power CW lasers because of the very low quantum yields. However, in a recent series of publications the ligand field photochemistry of Co(NH$_3$)$_6$$^{3+}$, Co(NH$_3$)$_5$(H$_2$O)$^{3+}$, Co(NH$_3$)$_5$F^{2+}, Co(NH$_3$)$_5$Cl^{2+}, *trans*-Co(en)$_2Cl_2$$^+$, *trans*-Co(cyclam)Cl$_2$$^+$, *cis*-Co(en)$_2Cl_2$$^+$, and of various Co(III) trien and tren complexes was reported in some detail.[4-7] Results for several of these complexes have been confirmed and extended to irradiations in the wavelength region of the presumed triplet absorption long wavelength shoulder on the first ligand field band.[7]

The results of the above studies indicate that the ligand field photochemistry of Co(III) ammines is stereospecific and often antithermal—where two kinds of ligands are present the one predominantly photoaquated is often not the thermally labile one. The importance of stereochemistry is especially evident in the observation that *cis*-α-Co(trien)Cl$_2$$^+$ and *cis*-β-Co(trien)Cl$_2$$^+$ differ by a thousandfold in their photoreactivity. Further, it was suggested that the low quantum yields (10^{-3} to 10^{-5}) were more a consequence of enhanced radiationless deactivation rates than of reduced excited state reactivity, relative to the corresponding Cr(III) species. Reaction was regarded as taking place from a thermally equilibrated excited (thexi) state and to amount to heterolytic bond fission at a labilized position. This last was determined by the same photolysis rules as have been important for Cr(III) photochemistry.[8] Since they are central to the present paper, their restatement here is relevant. Rule (1): For a complex having octahedral geometry, the axis which is photoactivated is the one containing ligands of weakest average ligand field strength. Rule (2): If the labilized axis contains ligands having different