Registry No. $Co_2(L\text{-dampa})_4O_2$, 40354-51-6; $[Co_2(L\text{-dampa})_4(O_2)(OH)]^-$, 40354-52-7; $[Co_2(l\text{-}1,2\text{-diaminopropane})_4(O_2)(OH)]^{3+}$, 40273-29-8; $[Co_2(L\text{-}2,4\text{-diaminobutyrate})_4(O_2)(OH)]^-$, 40354-53-8; H_2O_2, 7722-84-1.

Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Hydrolytic Reactions in Carbonate Systems Containing Tetradentate Macrocyclic (N_4) Complexes of Cobalt(III)[1]

JOHN F. ENDICOTT,* NOEL A. P. KANE-MAGUIRE, D. PAUL RILLEMA, and THOMAS S. ROCHE

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The mechanisms of base hydrolysis of bidentate carbonate have been examined in cobalt(III) complexes containing methyl-substituted tetradentate (nitrogen donor) macrocyclic ligands. The reactions have been found to proceed in two stages: (I) the formation of a ring-opened $Co(N_4)OHCO_3$ intermediate and (II) the formation of product *trans*-$Co(N_4)(OH)_2^+$. In the case that $N_4 = Me_6[14]dieneN_4$, $Co(N_4)OHCO_3$ could be generated in sufficient concentration that it could be partially characterized; the evidence suggests that this reaction intermediate is formed irreversibly and has a trans geometry. Acid hydrolysis of $Co(Me_6[14]dieneN_4)CO_3^+$ was found to be much slower than acid hydrolysis of $Co(Me_6[14]dieneN_4)OHCO_3$, making possible the determination of the relative concentrations of these complexes and permitting the isotopic composition of the ring-opened species to be determined in ^{13}C–^{18}O double-labeled tracer experiments. The latter experiments demonstrated that cobalt–oxygen bond breaking occurred in the ring-opening step. Three different isomeric tetramine complexes have also been examined. These complexes exhibited the same general pattern of reactivity in base hydrolysis as the $Co(Me_6[14]dieneN_4)CO_3^+$; however, for these $Co(Me_6[14]aneN_4)CO_3^+$ complexes the ring-opened intermediate did not reach a sufficient concentration to permit its characterization. It was possible to sample unreacted tetraamine carbonate in order to determine from an ^{18}O tracer study that there could be no labile ring-opening preequilibrium involving carbon–oxygen bond breaking in the base hydrolysis. The decarboxylation of the tetraamine complexes was found to be reversible both in acid and in base. The role of ligand stereochemistry in determining the net reactivity is discussed in terms of nucleophillic scavenging for a five-coordinate ring-opened intermediate. The plausibility of such a process was demonstrated in experiments which showed that the rate of acid hydrolysis varied markedly with the anionic composition of the medium.

Introduction

There have been few attempts to probe the relationships between ligand stereochemistry and the chemical reactivity of coordination complexes.[2] The methyl-substituted macrocyclic tetraamines prepared by Curtis[3–7] clearly have considerable potential for stereochemical alteration of reaction rate and possibly even reaction mechanism. In a previous study Kernohan and Endicott[8] argued that the inertness of $Co(C(5,12)\text{-}rac\text{-}Me_6[14]aneN_4)CO_3^{3+}$ [4] to acid hydrolysis most probably resulted from a stereochemical "protection"[9] of the bidentate carbonate group. This view of the observed, large variations in carbonate hydrolysis rates[10] has been elaborated by Dasgupta and Harris[11] and subjected to further critical evaluation and reinterpretation by Poon.[12]

The present study was originally undertaken to examine the significance of stereochemical factors in the base hydrolyses of bidentate carbonate. Preliminary observations[8] had indicated that the net hydrolysis rate in basic solution was similar for the $Co(en)_2CO_3^+$ [13,14] and $Co(C(5,12)\text{-}rac\text{-}Me_6[14]aneN_4)CO_3^+$ complexes although a number of details of their respective reactions appeared to be different. It was thus something of a paradox that due to steric interference with carbonate chelate ring opening the rates of

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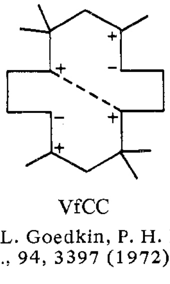
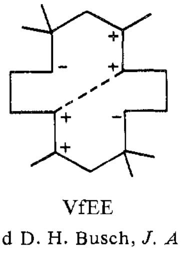
(2) For example see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

(3) N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

(4) In the present study we use a contracted form of the abbreviations proposed by Busch and coworkers[5] for these ligands. Thus $Me_6[14]dieneN_4$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; C(5,12)-*rac*-$Me_6[14]aneN_4$ = C(5,12)-*rac*-5,7,7,12,14,14-$Me_6[14]aneN_4$ = C(5,12)-*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; C(5,14)-*meso*-$Me_6[14]aneN_4$ = C(5,14)-*meso*-5,7,7,12,12,14-$Me_6[14]aneN_4$ = C(5,14)-*meso*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. The two different configurational isomers of the folded C(5,12)-*rac*-$Me_6[14]aneN_4$ ligand are distinguished by prefixes α (for VfCC[5,6]) and β (for VfEE[5,6]); see diagrams below (a plus sign at an asymmetric center indicates the H atom at the center lies above the plane of the flattened macrocycle; a dashed line indicates axis of folding)



VfCC



VfEE

(5) V. L. Goedkin, P. H. Merrell, and D. H. Busch, *J. Amer. Chem. Soc.*, 94, 3397 (1972).

(6) P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc. A*, 3397 (1971).

(7) N. A. P. Kane-Maguire, J. F. Endicott, and D. P. Rillema, *Inorg. Chim. Acta*, 6, 443 (1972).

(8) J. A. Kernohan and J. F. Endicott, *J. Amer. Chem. Soc.*, 91, 6977 (1969).

(9) In the original paper[8] this "protection" was considered to be thermodynamic, *i.e.*, the stability of the bidentate carbonate relative to the *cis*-aquocarbonato complexes.

(10) For a review see K. V. Krishnamurty, G. M. Harris, and V. S. Sastri, *Chem. Rev.*, 70, 171 (1970).

(11) T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, 93, 91 (1971).

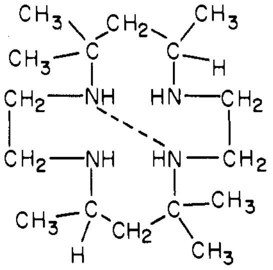
(12) C. K. Poon, *Coord. Chem. Rev.*, in press.

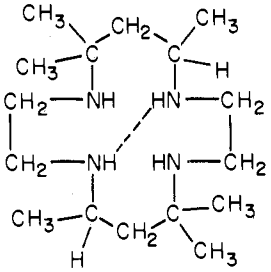
(13) M. E. Farago, *Coord. Chem. Rev.*, 1, 66 (1966).

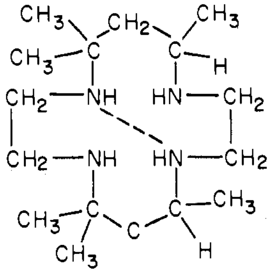
(14) D. J. Francis and R. B. Jordan, *J. Amer. Chem. Soc.*, 91, 6626 (1969).

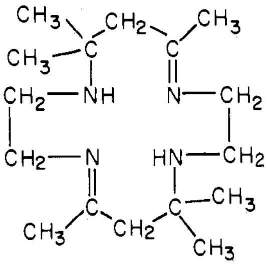
acid hydrolyses of $Co(en)_2CO_3^+$ and Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3^+ should differ by a factor of more than 10^4 while their base hydrolyses which may also involve a ring-opened intermediate,[8,10,12-14] were very similar in rate. A consequence of this contrast in reactivities is that the half-life for hydrolysis of Co(C(5,12)-*rac*-Me_6-[14]aneN_4)CO_3^+ is orders of magnitude shorter in 0.1 *M* base than in 0.1 *M* acid while the reverse is observed for $Co(en)_2CO_3^+$.

We have recently characterized two Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3^+ isomers.[7] We are thus able to compare stereochemical interactions in these two different isomers to those in Co(C(5,14)-*meso*-Me_6[14]aneN_4)CO_3^+ and Co(Me_6[14]dieneN_4)CO_3^+ and to contrast these systems to the previously investigated $Co(en)_2CO_3^+$ hydrolyses.


α-C(5,12)-*rac*-Me_6[14]aneN_4


β-C(5 12)-*rac*-Me_6[14]aneN_4


C(5,14)-*meso*-Me_6[14]aneN_4


Me_6[14]dieneN_4

Experimental Section

The preparation and characterization of Co(Me_6[14]dieneN_4)-CO_3^+,[15] the isomeric ligands C(5,12)-*rac*-Me_6[14]aneN_4 and C(5,14)-*meso*-Me_6[14]aneN_4, the configurational isomers α-Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3^+ [7] and β-Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3^+,[7] and the complex Co(C(5,14)-*meso*-M_6[14]aneN_4)CO_3^+ [7] are described in detail elsewhere.

The [α-*cis*-Co(C(5,12)-*rac*-Me_6[14]aneN_4)$(OH_2)_2$]$(ClO_4)_3$ was prepared by dissolving [α-Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3]ClO_4 in concentrated $HClO_4$. The blue crystals formed after the solution stood a few days in the refrigerator. The characterization of the complex is reported elsewhere.[7]

Standard spectrophotometric techniques were used to determine absorbances in a Cary 14 spectrophotometer.

All rate measurements were carried out on solutions maintained at constant temperature by the circulation of water from an external thermostat both through the walls of the cell compartment and through the glass jacket of the spectrophotometer cell.

Pmr measurements were made using Varian T-60 and/or A-60 spectrometers.

Samples of [Co(Me_6[14]dieneN_4)$^{13}CO_3$]ClO_4 were prepared by first adding 0.41 g of ^{13}C-enriched K_2CO_3 to a solution (adjusted to pH 3 with NaOH) of 2 g of [Co(Me_6[14]dieneN_4)$(OH_2)_2$]$(ClO_4)_3$ in 25 ml of water. The final solution pH was about 6.5. This solution was boiled briefly to dissolve the precipitate and then allowed to cool to room temperature. The $KClO_4$ precipitate was removed by filtration. Red crystals of the product formed from the filtrate over a 2-day period. These crystals were separated, pulverized, and boiled briefly with ethanol to remove water of crystallization.

We prepared and transferred most of the solutions for the tracer studies in the CO_2-free nitrogen atmosphere of a glove box. We used NaOH solutions to purge the glove box atmosphere of CO_2. In a typical experiment 0.150 g of solid [Co(Me_6[14]dieneN_4)^{13}-CO_3]ClO_4 was weighed into a 25-ml volumetric flask. The flask was transferred to the inert atmosphere of the glove box and filled to a volume with 25 ml of ^{18}O-enriched water. After the solid had dissolved, 0.25 ml of standardized 10.1 *M* NaOH was syringed into the flask and the solution was transferred to the quenching cell. This cell was composed of two compartments, each fabricated from a round-bottomed flask and connected by a ball joint, one compartment for the reacting solution and the other for an acid. The volume of acid solution used was 0.3 ml. The cell was sealed, then removed from the nitrogen atmosphere, attached to a vacuum rack, and evacuated after 10-min contact with the base. The base hydrolysis reaction was quenched by mixing reactant and acid solutions after 15 min. The CO_2 recovered was transferred, using a Toepler pump, to a sample cell containing a known amount of argon. Isotopic composition of the gaseous sample was determined mass spectrometrically. In tracer experiments with Co(α-C(5,12)-*rac*-Me_6[14]aneN_4)CO_3^+, where the isotopic composition of the unreacted substrate was monitored, less elaborate precautions were used. A CO_2-purged N_2 stream was passed through solutions during preparation and reaction. Base hydrolysis was carried out to ~50% completion in 0.1 *M* NaOH at 60°. The reactant solution was then acidified to pH 1 and [Co(α-C(5,12)-*rac*-Me_6[14]aneN_4)CO_3]ClO_4 was collected. This solid was then treated with concentrated $HClO_4$ *in vacuo* and CO_2 was collected and analyzed as before.

Results and Discussion

A. General Observations. In strongly basic solution hydrolyses of the macrocyclic carbonate complexes produce the corresponding *trans*-dihydroxy complexes. We obtained spectroscopic evidence that an intermediate builds up during the early stages of the hydrolysis of Co(Me_6[14]dieneN_4)-CO_3^+ and α-Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3^+; this evidence is similar to that obtained for the analogous Co(en)CO_3^+ hydrolysis.[13,14] In contrast, our studies of the hydrolysis of β-Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3^+ and Co(C(5,14)-*meso*-Me_6[14]aneN_4)CO_3^+ have provided no evidence which may be interpreted as the buildup of a ring-opened intermediate.

The formation of carbonato complexes from Co^{III}(Me_6-[14]aneN_4)X_2 species proceeds more readily than do the carbonate hydrolyses under mild conditions. This kind of behavior appears to be unique to this family of complexes. We have found these systems to be both fascinating and nearly intractable. It is important to recall that the *cis*-Co^{III}(C(5,12)-*rac*-Me_6[14]aneN_4)X_2 and *cis*-Co^{III}(C(5,14)-*meso*-Me_6[14]aneN_4)X_2 complexes seem to be metastable species with varying lifetimes.[7] Thus our efforts to make detailed quantitative examinations of the hydrolyses of the Co(N_4)CO_3^+ complexes have generally been frustated by the instabilities and complex reactivities of the initial hydrolysis products, by the insolubilities of the perchlorate salts of the Me_6[14]aneN_4 carbonato complexes, and by the tendency of these complexes to coordinate with NO_3^-.[16] We have included in this report some semiquantitative and qualitative observations on the behavior of these tetramine complexes. These observations lead to partial understanding of the systems; complete understanding has not been achieved, because the complexity of the systems prevented extensive quantitative measurements.

B. Base Hydrolysis of Co(Me_6[14]dieneN_4)CO_3^+. We found this system to be relatively free of complications and our observations help establish several important mechanistic points.

Examination of the absorption spectra of the carbonate and *trans*-dihydroxy complexes indicated that a simple de-

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(15) N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, 6, 770 (1967).

(16) P. O. Whimp and N. F. Curtis, *J. Chem. Soc. A*, 1827 (1966).

Table I. Kinetic Parameters for Base Hydrolysis of Bidentate Carbonate in $Co(N_4)CO_3^+$ Complexes (Stage I, Ring Opening)

N_4	μ^a	T, °C	10^4k_1, sec^{-1}	10^3k_2, M^{-1} sec^{-1}	10^3k_3, M^{-2} sec^{-1}	E_a, kcal/mol
$Me_6[14]dieneN_4$[b]	1.0 (3)	10	0.0 ± 0.2	0.8 ± 0.2	~0.4	
	1.0 (8)	14	0.1 ± 0.1	1.6 ± 0.2	2.3 ± 0.5	
	1.0 (3)	15	0.4 ± 0.4	1.5 ± 0.5	~2	
	1.0 (2)	25	~0	4 ± 1[c]		
	1.0[d]					24 ± 2
	1.0[e]					24 ± 3
α-C(5,12)-*rac*-$Me_6[14]aneN_4$[f]	0.005[g] (5)	25		0.66[h]		
	0.01[g]			2.2[h]		
	0.08[g]			6.6[h]		
	0.25[g]			3.8[h]		
	0.50[g]			3.4[h]		

[a] $NaClO_4$, NaOH. Number of determinations in parentheses. [b] [Co(III)] = 4.8×10^{-4} *M*; initial reaction stage observed at 325 nm. [c] For $[OH^-] = 0.10$ *M*, $k_{obsd} = 8.4 \times 10^{-4}$ sec^{-1}, and for $[OH^-] = 0.20$ *M*, $k_{obsd} = 16.5 \times 10^{-4}$ sec^{-1}. [d] For k_{obsd} with $[OH^-] = 0.10$ *M*. [e] For k_{obsd} with $[OH^-] = 0.20$ *M*. [f] [Co(III)] = 5.86×10^{-4} *M*; initial stage of reaction observed at 325 nm. [g] NaOH only. [h] k_{obsd}; $A'_{max} = 0.66 \pm 0.04$ independent of $[OH^-]$.

carboxylation reaction to form *trans*-$Co(Me_6[14]aneN_4)(OH)_2^+$ should result in isosbestic points at 404, 455, and 579 nm. However we found that the *trans*-dihydroxy complex is formed in two stages, I and II. The initial reaction spectra (Figure 1) showed isosbestic points at 402, 454, and 576 nm (as expected for the simple decarboxylation reaction) and, in addition, one at 349 nm. This last isosbestic point is associated with an initial rise in absorbance at wavelengths shorter than 350 nm. Very similar observations were made for the base hydrolysis of the corresponding ethylenediamine complex, $Co(en)_2CO_3^+$.[13,14] By analogy with the latter system, the initial absorbance increase below 350 nm might be interpreted as being caused by the production of *cis*-$Co(Me_6[14]dieneN_4)OHCO_3$. The presence of isosbestic points at 402, 454, and 576 nm during this initial stage would require *trans*-$Co(Me_6[14]dieneN_4)(OH)_2^+$ and the ring-opened species to have similar spectra in this region.

1. Stage I, Ring Opening. The kinetics of the initial step can be treated as pseudo first order following the approach of Francis and Jordan.[14] We can fit the pseudo-first-order rate constants to the three-term expression $k_{obsd} = k_1 + k_2[OH^-] + k_3[OH^-]^2$. Values of the corresponding kinetic parameters are listed in Table I. The zero-order term, k_1, is probably not significant outside of experimental error (see Figure 2). In the method of Francis and Jordan,[14] the absorbance at equilibrium, A'_{max}, for the initial step may be obtained by extrapolation or by finding a value which linearizes a first-order plot. Similar values were obtained by both methods, and the values of A'_{max} were found to increase with $[OH^-]$ and to decrease slightly with temperature (constant $[OH^-]$) as for $Co(en)_2CO_3^+$. From the $[OH^-]$ dependence of A'_{max} we might infer an equilibrium constant for the ring-opening step (1) of $K_1 = 12 \pm 3$ M^{-1} at 14°. Unfortunately this analysis

$$Co(Me_6[14]dieneN_4)CO_3^+ + OH^- \overset{K_1}{\rightleftarrows} Co(Me_6[14]dieneN_4)OHCO_3 \qquad (1)$$

of the kinetic data is not unequivocal since the observed rate law for ring opening is very different from that obtained by Francis and Jordan. For example since the inferred value of K_1 is so small and since the ratio of k_{obsd}(stage I)/k_{obsd}(stage II) increases as $[OH^-]$ increases, the apparent increased buildup of ring-opened intermediate may only be the kinetic result of the change in the competition between stages I and II. Fortunately, in the present system a more critical means of examining (1) is available since the rate of acid hydrolysis of $Co(Me_4[14]aneN_4)CO_3^+$ is small.[8] Thus it should be possible to find a concentra-

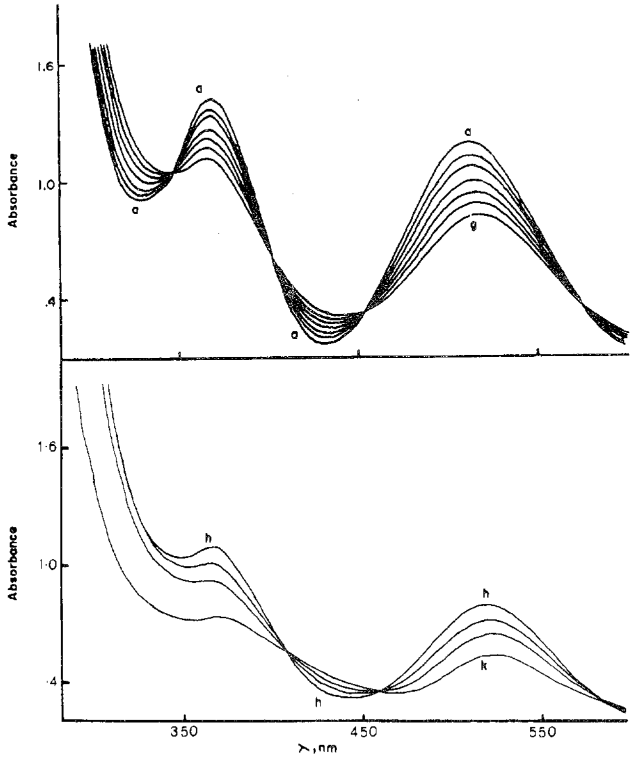

Figure 1. Changes in absorption spectrum of $Co(Me_6[14]dieneN_4)CO_3^+$ during base hydrolysis. Changes observed over a 10-hr period (from a to k) at 25° in 0.1 *M* NaOH. Upper figure for stage 1 (a-g recorded during a 1-hr period); lower figure for stage II (h-j recorded in 1 hr).

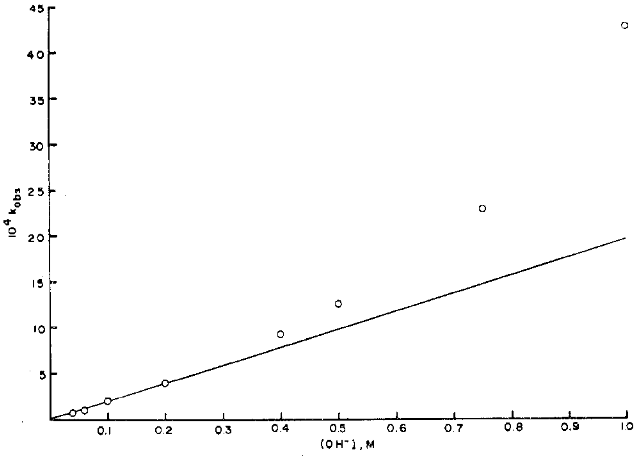

Figure 2. Hydroxide dependence of k_{obsd} for stage I of the hydrolysis of $Co(Me_6[14]dieneN_4)CO_3^+$ at 14° (see Table I).

tion of acid such that acidification of an apparently "equilibrated" (with respect to stage I) solution of $Co(Me_6[14]dieneN_4)CO_3^+$ in base will not result in appreciable hydrolysis of the bidentate carbonate, while very rapidly hydrolyzing the monodentate carbonate.[10,17] In each of the two experiments described in Table II the base hydrolysis reaction was run to about 3 half-lives of stage I and then quenched with $HClO_4$. If (1) were indeed a preequilibrium with $K_1 \simeq 11$, then only about 50% of the cobalt(III) should have been in the ring-opened form; however, the observed percentage conversion to intermediate is very close to the 87% expected for 3 half-lives of an irreversible ring-opening step.

Since stage I corresponded to the buildup in concentration of a reactive intermediate and since this intermediate underwent acid hydrolysis at a rate many orders of magnitude larger than $Co(Me_6[14]dieneN_4)CO_3^+$, we infer that the intermediate was a ring-opened carbonate species as indicated in (1). However, the final reaction product was *trans*-$Co(Me_6[14]dieneN_4)(OH)_2^+$, so we must consider whether the ring-opened intermediate was of cis or trans geometry. The single piece of evidence which suggests that this intermediate might have been of a cis geometry is that the Co^{III}–OCO_2^- bond appeared to remain intact during (1). On the other hand there are several considerations which are most consistent with a trans geometry for the intermediate in question: (1) the ring-opening step appeared to be irreversible; (2) relatively large absorbance changes were observed during stage I; (3) *cis*-$Co(Me_6[14]dieneN_4)(OH_2)_2^{3+}$ has a half-life of about 4 min at 9.8° and 3 M $HClO_4$, conditions for which α-*cis*-Co(C(5,12)-*rac*-$Me_6[14]aneN_4)(OH_2)_2^{3+}$ has a half-life of many hours;[7] (4) the half-life for cis → trans isomerization of α-*cis*-Co(C(5,12)-*rac*-$Me_6[14]aneN_4)(OH_2)_2^{3+}$ decreased as pH increased;[7] (5) we have never detected the *cis*-dihydroxy species and in fact have found all *cis*-$Co^{III}(C(5,12)$-$Me_6[14]aneN_4)X_2$ complexes in which X is anionic to have only transient existences;[7,18] (6) in addition to considerations of charge, which appear to play a role of some kind in the cis → trans isomerization of these complexes, the monodentate carbonate ligand is relatively bulky and on this basis alone the *cis*-hydroxycarbonato complexes would be expected to isomerize more readily than a dihydroxy complex.

In view of these considerations we do not believe that a cis geometry is reasonable for the ring-opened intermediate, which we found to have a lifetime greater than 30 min (1.0 M OH^-, 14°) dependent only on $[OH^-]$ (or temperature). We therefore propose the following as the predominant mechanism, at low $[OH^-]$, for the ring-opening step in $Co(Me_6[14]dieneN_4)CO_3^+$

$$Co(N_4)CO_3^+ + OH^- \underset{k_{-r}}{\overset{k_r}{\rightleftarrows}} cis\text{-}Co(N_4)OHCO_3 \tag{2}$$

$$cis\text{-}Co(N_4)OHCO_3 \xrightarrow{k_i} trans\text{-}Co(N_4)OHCO_3 \tag{3}$$

We have examined the possibility of solvent oxygen-coordinated carbonate oxygen exchange during the ring-opening step. In these experiments we monitored the amount of CO_2 recovered by mixing the evolved gas with a known aliquot of argon. Stage I for the hydrolysis of $Co(Me_6[14]dieneN_4)CO_3^+$ in 0.1 M NaOH (no added $NaClO_4$) and $H_2{}^{18}O$-enriched water was quenched after 15 min (3 half-lives) with acetic acid; HO_2CCH_3 was used to ensure that there was no acid hydrolysis during removal of CO_2 from solution. In these experiments we recovered 60–80% of the original coordinated carbonate as CO_2, consistent with the irreversibility of (1) implied by data in Table II and with the difficulty of quantitatively recovering CO_2 from solutions of relatively high pH.

Table II. Determination of Yield of Intermediate in Stage I for $Co(Me_6[14]diene)CO_3^+$

Quantity determined	Expt A	Expt B
Ionic strength	1.0	1.0
$[OH^-]$, M	0.10	0.10
Temp, °C	25	25
Initial $[Co(III)] \times 10^3$, M	4.86	4.84
Reaction duration, min	42.5	45
Final $[H^+]$, M	0.05	0.02
Absorbance[a]		
(i) at 440 nm	0.183	0.183
(ii) at 480 nm	0.105	0.103
$[Co(N_4)CO_3^+] \times 10^3$,[b] M	0.84	0.81
$[trans\text{-}Co(N_4)(OH_2)_2^{3+}] \times 10^3$,[b] M	4.02	4.03
Cor for acid hydrolysis $\times 10^3$,[c] M	<0.34	<0.13
% conversion to intermediate	76–83	81–83

[a] Absorbance measured less than 4 min after quenching the base hydrolysis reaction with acid. [b] At 440 and 480 nm the molar absorptivities of $Co(Me_6[14]dieneN_4)CO_3^+$ are 19.9 and 77.0, respectively; and 41.4 and 10.1, respectively, for *trans*-$Co(Me_6[14]dieneN_4)(OH_2)^{3+}$. [c] Data in ref 7, extrapolated to $\mu = 1.0$, give $k_{obsd} = 0.0116[H^+]$ sec^{-1}.

The exchange experiments were performed with ^{13}C-enriched (~50%) carbonate in order that we might minimize errors due to carbonate dissolved in water or in the basic solutions. The differences in the 46/44 and 47/45 values of m/e ratios can be attributed to the presence of some free carbonate in the reactant solution (see especially experiments 3 and 6–8, Table III). The variations in the 45/44 ratio reflect different samples (and preparations) as well as some fluctuation in the amount of CO_2 dissolved in reactant solutions. Although the 47/45 ratio is insensitive to dissolved CO_2, it is necessary to take account of the background (experiment 7) and the significant amounts of "method-induced" exchange of CO_2 and $H_2{}^{18}O$ in acidic solution (experiments 1, 4, and 8) under our experimental conditions, the latter presumably through the hydration–dehydration reactions of CO_2.[19] Under our conditions we obtained a background exchange of 20 ± 5% in acidic solutions. Experiments 3 and 6 (Table III) indicate 25 ± 5% total exchange observed in the ring-opening step, stage I, of the base hydrolysis $Co(Me_6[14]dieneN_4)CO_3^+$. These tracer experiments establish that the ring-opening step proceeds, at $[OH^-] = 0.1$ M, predominantly (82–98%) in a process which breaks the cobalt(III)–oxygen bond of the bidentate carbonate. Under these experimental conditions, the ring-opening reaction proceeds about 88% through the path first order in $[OH^-]$. The small amount of exchange we did observe is probably not significant over the observed background exchange, but it could also be consistent with oxygen exchange in the ring-opening path which is second order in $[OH^-]$. Thus the path second order in $[OH^-]$ could involve carbon–oxygen bond breaking, nucleophilic attack on carbon, or nucleophilic scavenging for a five-coordinate conjugate base intermediate. We have

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(17) T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, **90**, 6360 (1968).

(18) N. A. P. Kane-Maguire and J. F. Endicott, unpublished observations.

(19) J. T. Edsall in "CO_2: Chemical, Biochemical and Physiological Aspects," R. E. Forster, J. T. Edsall, A. B. Otis, and F. J. W. Roughton, Ed., Document NASA SP-188, U. S. Government Printing Office, Washington, D. C., 1969, p 15.

Table III. Tracer Studies of Solvent-Carbonate Oxygen Exchange for $Co(N_4)CO_3^+$

		Oxygen exchange during stage I				
		m/e ratios for isotopic CO_2 species				
		Obsd				
Expt[a]	CO_2 collected, mol × 10^{-4}	45/44	46/44	47/45	Max 47/45[b]	% exchange[c]
1. $K_2{}^{13}CO_3 \cdot xH_2O$ + 1 *M* $HClO_4$		1.21	0.028	0.025	0.10	23
2. $K_2{}^{13}CO_3 \cdot xH_2O$ + 0.1 *M* NaOH (45 min); $HClO_4$ quench		0.925	0.065	0.064	0.0975	66
3. $Co(N_4)^{13}CO_3^+$ + 0.1 *M* NaOH; HO_2CCH_3 quench	1.87	1.031	0.044	0.031	0.0950	30
4. $Co(N_4)^{13}CO_3^+$ + 0.1 *M* $HClO_4$		1.28	0.018	0.016	0.0925	14
5. $NaHCO_3$ + $H_2{}^{18}O$ (24 hr); $HClO_4$ quench			0.091		0.090	101
6. $Co(N_4)^{13}CO_3^+$ + 0.1 *M* NaOH; HO_2CCH_3 quench	2.37	1.026	0.024	0.019	0.0825	19
7. $Co(N_4)^{13}CO_3^+$ + 0.1 *M* $HClO_4$[d]		1.28	0.0058	0.0048		
8. $Co(N_4)^{13}CO_3^+$ + 0.1 *M* $HClO_4$[e]		1.37	0.013	0.011	0.030	25
9. $NaCO_3$ + 9 *M* $HClO_4$[f]			0.0040		(0.032)[g]	0
10. $[Co(N_4)CO_3]ClO_4$[h] + 9 *M* $HClO_4$[f]			0.0041		(0.032)[g]	0
11. $[Co(N_4)CO_3]ClO_4$[h,i] + 12 *M* $HClO_4$			0.0052		(0.040)[g]	0

[a] All reactions run in solutions about 5% enriched in $H_2{}^{18}O$, except as indicated; 3.1 × 10^{-4} mol of carbonate salt or complex was used in experiments indicated. $(N_4) = Me_6[14]dieneN_4$ except as indicated. [b] Values corrected for dilution in successive experiments. Values for experiments 1-6 are referenced against that for experiment 5. [c] Based on the value of the observed fraction exchange to the maximum possible fraction exchange. Fraction exchange = $R/(1 + R)$ where R is the 47/45 ratio of *m/e* ratios. Values of R were corrected for background 47/45 ratio as observed in experiment 7. [d] Normal water. [e] Solution 1.5% enriched in $H_2{}^{18}O$. [f] Solution 1.6% enriched in $H_2{}^{18}O$. [g] Estimated 46/44 value of *m/e* ratios. [h] (N_4) = C(5, 12)-*rac*-$Me_6[14]aneN_4$. [i] Sample of unreacted material from 50% hydrolysis of $Co(N_4)CO_3^+$[h] in 0.1 *M* NaOH (4% enriched with $H_2{}^{18}O$) at 60°.

Table IV. Kinetic Parameters for Base Hydrolysis of Bidentate Carbonate in $Co(N_4)CO_3^+$ Complexes (Stage II)

N_4	μ[a]	T, °C	$10^4 k_4$, sec^{-1}	$10^4 k_5$, M^{-1} sec^{-1}	E_a, kcal/mol
$Me_6[14]dieneN_4$[b]	1.00 (5)	25	0.72 ± 0.1	4.2 ± 0.4	
	(5)	35	2.4 ± 0.3	12 ± 1	
	(5)	45	7.8 ± 1	31 ± 3	
α-C(5,12)-*rac*-$Me_6[14]aneN_4$[c]	0.125 (3)	50	0.4 ± 0.1[d]	150 ± 15[d]	23 ± 1[e]
β-C(5,12)-*rac*-$Me_6[14]aneN_4$[c]	0.125 (7)	50	0.4 ± 0.1[d]	150 ± 15[d]	22 ± 1[e]
C(5,14)-*meso*-$Me_6[14]aneN_4$[c]	0.125 (5)	50	0.5 ± 0.1[d]	110 ± 12[d]	23 ± 1[e]

[a] $NaClO_4$, NaOH. [b] [Co(III)] = 2.4 × 10^{-3} *M*. [c] [Co(III)] = 5.8 × 10^{-4} *M*. [d] Initial rates were used at low $[OH^-]$. [e] For k_{obsd} at $[OH^-]$ = 0.125 *M*. Determinations made in 5° intervals from 35 to 50°.

not found a means of distinguishing among these possibilities.

2. Stage II, Decarboxylation. After the initial ring-opening stage, and with $[OH^-] > 0.03\ M$, the base hydrolysis of $Co(Me_6[14]dieneN_4)CO_3^+$ proceeds smoothly to form the *trans*-dihydroxy complex (Figure 1). Thus stage II of the base hydrolysis appears to be decarboxylation of the complex. Kinetic data for this second stage of the reaction are summarized in Table IV. Once again the pseudo-first-order rate constants obtained from the observed absorbance changes are strongly dependent on $[OH^-]$; the observations are well represented by $k'_{obsd} = k_4 + k_5[OH^-] + k_6[OH^-]^2$ (see Figure 3). In this case the $[OH^-]$-independent term is relatively large and well defined while the second-order term in $[OH^-]$ is small, only being exhibited at high $[OH^-]$, and likely corresponds to a variation of the activity coefficient of hydroxide as $[OH^-] \to 1\ M$.[20] The rate law for this reaction stage is consistent with simple dissociative hydrolytic reactions; *e.g.*, (4) and (5), and (6) and (7) could

$$trans\text{-}Co(N_4)OHCO_3 \rightarrow \underset{\text{II}}{\left\{trans\text{-}Co(N_4)OH^{2+}\right\}} + CO_3{}^{2-} \qquad (4)$$

$$\text{II} + OH^- \xrightarrow{\text{fast}} trans\text{-}Co(N_4)(OH)_2{}^+ \qquad (5)$$

$$trans\text{-}Co(N_4)OHCO_3 + OH^- \xrightarrow{k_{CB}} \underset{\text{III}}{\left\{trans\text{-}Co(N_4\text{-}H^+)OH^+\right\}} + CO_3{}^{2-} + H_2O \qquad (6)$$

$$\text{III} + H_2O \xrightarrow{\text{fast}} trans\text{-}Co(N_4)(OH)_2{}^+ \qquad (7)$$

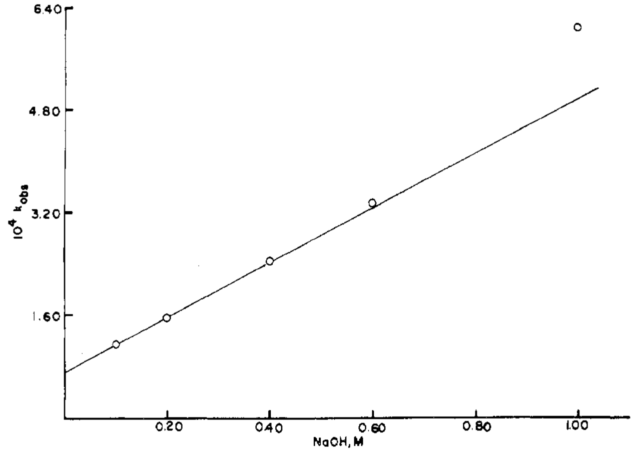

Figure 3. Hydroxide dependence of k_{obsd} for stage II of the hydrolysis of $Co(Me_6[14]dieneN_4)CO_3^+$ at 25° (see Table IV).

account for the zero-order and first-order terms in $[OH^-]$, respectively (note that (6) involves deprotonation of a ligand amine and has considerable precedent among the *trans*-$Co^{III}(N_4)X_2$ (X = halide) complexes[2,12,21-23]). The much larger value of k_4 for $Co(Me_6[14]dieneN_4)CO_3^+$ than for the tetramine complexes is consistent with some stabili-

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(20) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold, New York, N. Y., 1958.

(21) J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, **9**, 1504 (1970).

(22) D. P. Rillema and J. F. Endicott, to be submitted for publication.

(23) M. L. Tobe, *Accounts Chem. Res.*, **3**, 337 (1970).

zation of a five-coordinate intermediate by the unsaturated ligand (see ref 8, 21, and 22 for discussions of this point).

C. Base Hydrolysis of the Carbonato-Tetramine Complexes. 1. Stage I. Similar to $Co(en)_2CO_3^+$ and $Co(Me_6\text{-}[14]dieneN_4)CO_3^+$, we observed the absorbance at 320 nm to increase following the mixing of α-Co(C(5,12)-*rac*-$Me_6[14]aneN_4)CO_3^+$ with base and then to decrease much more slowly. Interpretation of this observation is ambiguous because the absorbance in the 320-nm spectral region is temperature sensitive (ϵ_{320} increases about 30% between 25 and 50°) for both the α- and β-Co(C(5,12)-*rac*-$Me_6[14]aneN_4)CO_3^+$ complexes, the carbonato complexes are extraordinarily stable, and the perchlorate salts are sparingly soluble. The temperature-dependent absorbance probably results from differing distributions of ligand conformational isomers (*e.g.*, chair and boat forms of the six-membered chelate rings) and should not preclude analysis of chelate ring opening.

The stability of the Co(C(5,12)-*rac*-$Me_6[14]aneN_4)CO_3^+$ complexes (see section D) does present some troublesome problems. For example acidification of a solution containing Co(C(5,12)-*rac*-$Me_6[14]aneN_4)OHCO_3$ cannot be expected to give a reliable estimate of the ring-opened intermediate since Co(C(5,12)-*rac*-$Me_6[14]aneN_4)CO_3^+$ is appreciably more stable than *cis*-Co(C(5,12)-*rac*-$Me_6\text{-}[14]aneN_4)(OH_2)_2^{3+}$. Thus acidification of a solution which had been allowed to react with OH^- until the 320-nm absorbance reached a maximum gave evidence for only a 6–10% (depending on whether one assumes the product is *trans*- or *cis*-Co(C(5,12)-*rac*-$Me_6[14]aneN_4)\text{-}(OH_2)_2^{3+}$) decrease in [α-Co(C(5,12)-*rac*-$Me_6[14]aneN_4)\text{-}CO_3^+$]. From our kinetic data we estimate that 6% of the carbonato complex had been converted to *trans*-Co(C(5,12)-*rac*-$Me_6[14]aneN_4)(OH)_2^+$ in the elapsed time period.

A few observations on the kinetics of the apparent ring-opening step for this complex are summarized in Table I and a typical kinetic plot is shown in Figure 4. We have been unable to control ionic strength in these studies due to the insolubility of the carbonato perchlorate. These data indicate that k_{obsd} for stage I of the base hydrolysis of α-Co(C(5,12)-*rac*-$Me_6[14]aneN_4)CO_3^-$ is strongly dependent on $[OH^-]$ (we have found that k_{obsd} decreases as ionic strength increases for these complexes); but the values of A'_{max} inferred from the Francis and Jordan[14] treatment of the primary kinetic data turn out to be independent of $[OH^-]$, possibly due to the ionic strength variation. We have been unable to find spectroscopic evidence for a ring-opened intermediate in the base hydrolysis of β-Co(C(5,12)-*rac*-$Me_6[14]aneN_4)CO_3^+$ and Co(C(5,14)-*meso*-$Me_6[14]aneN_4)CO_3^+$.

We have used the remarkable stability of α-Co(C(5,12)-*rac*-$Me_6[14]aneN_4)CO_3^+$ in acidic solution to determine whether any labile preequilibrium step occurs in the hydrolysis which might lead to exchange of solvent oxygen and coordinated carbonate oxygen. In experiment 11 of Table III, the complete hydrolysis of a sample of this complex was allowed to proceed through 1 half-life for stage II in ~4.0% ^{18}O-enriched 0.1 *M* NaOH solution. The solution was then cooled and acidified to pH 1 with $HClO_4$. The unhydrolyzed material which precipitated was collected and hydrolyzed with 12 *M* $HClO_4$ in an evacuated cell. The CO_2 collected from this sample showed no significant enrichment. This indicates that if stage I is a ring-opening step, it occurs through Co–O bond cleavage.

2. Stage II. The kinetics of the second stage of hydrolysis for these complexes was complicated. At relatively high $[OH^-]$ the observed absorbance changes were as expected for pseudo-first-order kinetic behavior (Figure 5) and reasonable isosbestic points, corresponding to conversion of a carbonato to a *trans*-dihydroxy complex (as in part C1), were observed (Figure 6). At lower $[OH^-]$ (*e.g.*, less than 0.05 *M*) the pseudo-first-order kinetic plots exhibited appreciable positive curvature which could be fit to the two stages (IIA and IIB) of successive pseudo-first-order reactions (Figures 7 and 8). Alternatively this curvature could be ascribed to the approach to equilibrium of a reversible reaction. Experiments described in section D provide evidence that the latter possibility is more likely.

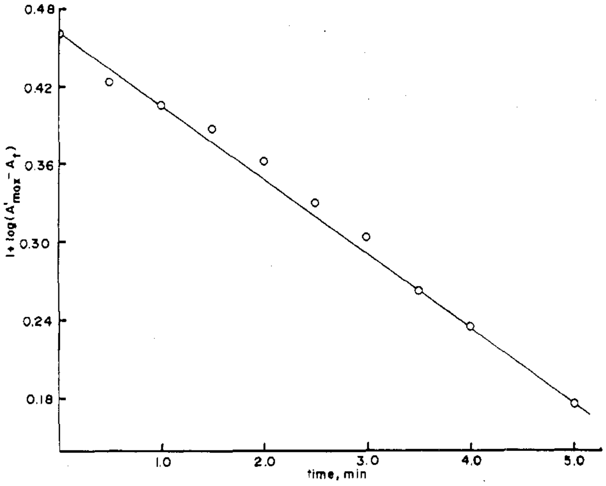

Figure 4. Approximate pseudo-first-order kinetic plot of absorbance changes (at 320 nm) during "stage I" of the base hydrolysis of α-Co(C(5, 12)-*rac*-$Me_6[14]aneN_4)CO_3^+$ in 0.0114 *M* NaOH at 25°.

Our data for α-Co(C(5,12)-*rac*-$Me_6[14]aneN_4)CO_3^+$ are qualitatively similar to the data for the β isomer (note that the observed rate constants of the α and β configurational isomers are nearly identical) but do not permit a useful estimate of kinetic parameters.

Owing to the relative insolubility of the $[Co(N_4)CO_3]\cdot ClO_4$ salts we have been unable to carry out studies at high ionic strengths so that the values cited for the $[OH^-]$-dependent terms of k_{obsd} may contain an appreciable contribution from variation of the acidity coefficients of hydroxide as $[OH^-] \to 0.125$ *M*.[20] However the hydroxide dependence of k_{obsd} cannot be only due to unaccounted activity changes since this term carries about 30% of the observed reaction even at $[OH^-] = 0.01$ *M*.

D. Reactions of α-Co^{III}(C(5,12)-*rac*-$Me_6[14]aneN_4)X_2$ with CO_2, HCO_3^-, and CO_3^{2-}. We have made some qualitative studies of the reverse of the hydrolysis reactions under various conditions. Since α-Co(C(5,12)-*rac*-$Me_6\text{-}[14]aneN_4)CO_3^+$ can be most easily prepared, most of our studies have been made on the α-*cis*-Co(C(5,12)-*rac*-$Me_6\text{-}[14]aneN_4)(OH_2)_2^{3+}$ and α-*trans*-Co(C(5,12)-*rac*-$Me_6\text{-}[14]aneN_4)Cl_2^+$ derivatives. The β-Co^{III}(C(5,12)-*rac*-$Me_6[14]aneN_4)X_2$ and the Co^{III}(C(5,14)-*meso*-$Me_6[14]\text{-}aneN_4)X_2$ complexes exhibit qualitatively similar behavior.

Our most surprising observation was that α-*cis*-Co(C(5,12)-*rac*-$Me_6[14]aneN_4)(OH_2)_2^{3+}$ *fixed* CO_2 in acidic solution! We have performed this experiment in two slightly different ways. In one experiment [α-*trans*-Co(C(5,12)-*rac*-$Me_6[14]aneN_4)Cl_2]ClO_4$ was warmed very gently (excessive heating causes decomposition of these complexes[7]) with 2 equiv of 0.1 *M* $AgNO_3$, the AgCl was removed by filtration, and the filtrate was diluted to 50 ml with $HClO_4$ (final [Co(C(5,12)-*rac*-$Me_6[14]aneN_4)(OH_2)_2^{3+}$] = 1.5×10^{-3} *M*; final solution $[H^+] = 0.3$ *M*). This procedure

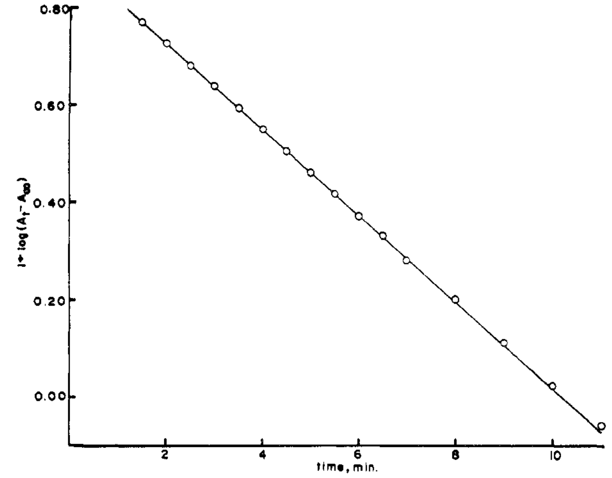

Figure 5. Pseudo-first-order treatment of absorbance changes (360 nm) during stage II of the base hydrolysis of β-Co(C(5, 12)-*rac*-Me_6[14]aneN_4)CO_3^+ in 0.125 *M* NaOH at 50°.

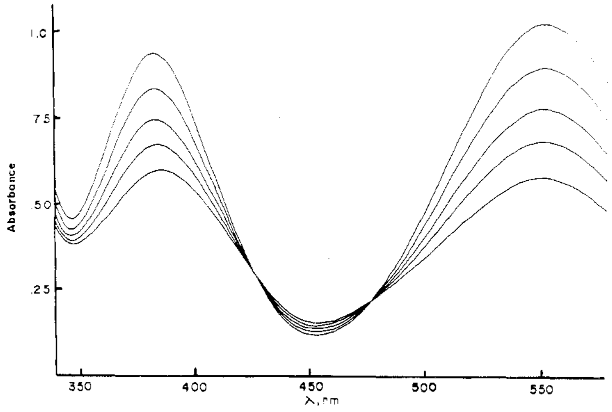

Figure 6. Changes in absorption spectrum of β-Co(C(5, 12)-*rac*-Me_6[14]aneN_4)CO_3^+ during base hydrolysis at 50° in 0.025 *M* NaOH (μ = 0.125). Original substrate was strongly absorbing at 550 and 380 nm; observations covered a time span of 35 min.

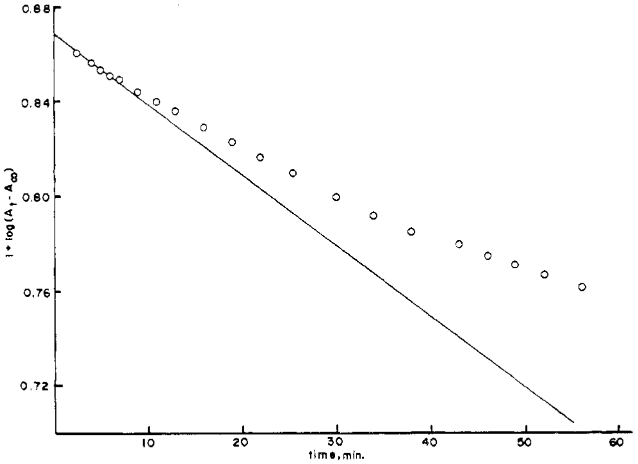

Figure 7. Pseudo-first-order plot illustrating the two components of stage II in the base hydrolysis of β-Co(C(5, 12)-*rac*-Me_6[14]aneN_4)-CO_3^+ in 0.005 *M* NaOH at 50°.

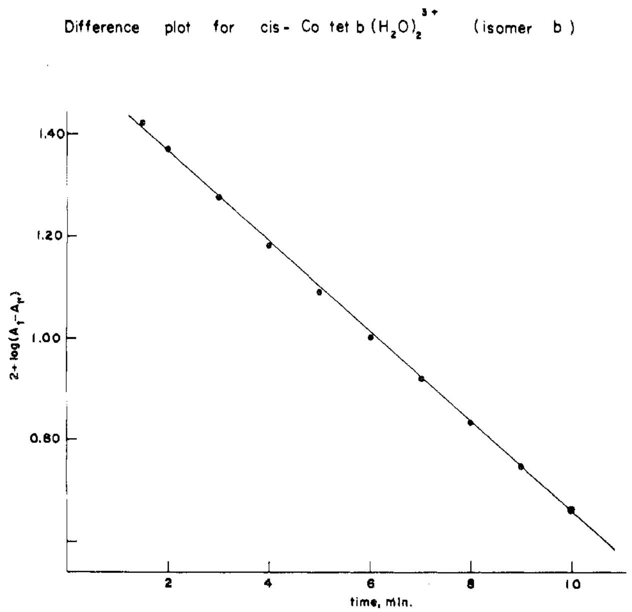

Figure 8. Pseudo-first-order plot of the initial stage of the reaction in Figure 7. Absorbances obtained by graphically subtracting changes due to the slower reaction.

gives a mixture of Co(C(5,12)-*rac*-Me_6[14]aneN_4)$(OH_2)_2{}^{3+}$ isomers of which at least 50% is α-*cis*-Co(C(5,12)-*rac*-Me_6-[14]aneN_4)$(OH_2)_2{}^{3+}$.[24] Tank CO_2 was presaturated with H_2O and then bubbled through a sample of this final solution. About 75% of the cobalt(III) originally present precipitated as [Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3]ClO_4 within 6 hr. In a control experiment no precipitate occurred when an identical sample of the acidic solution of Co(C(5,12)-*rac*-Me_6[14]aneN_4)$(OH_2)_2{}^{3+}$ was kept in an argon atmosphere for 6 hr.

In a second set of experiments, 0.028 g of [α-*cis*-Co(C-(5,12)-*rac*-Me_6[14]aneN_4)$(OH_2)_2$]$(ClO_4)_3$ was dissolved in 50 ml of 0.6 *M* $HClO_4$. After about 2 hr of bubbling H_2O-saturated CO_2, about 75% of the cobalt had precipitated as [Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3]ClO_4. The control experiments under argon again showed no sign of precipitate (it should be noted that some decrease in visible absorption occurred in both control experiments, presumably due to cis → trans isomerization[7]).

We have further found that [α-Co(C(5,12)-*rac*-Me_6[14]-aneN_4)CO_3]ClO_4 dissolved slightly in 0.60 *M* $HClO_4$. The visible absorption spectrum of the final solution suggested that the species in solution was predominantly Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3^+; however, a relatively high absorptivity in the near-ultraviolet spectrum implied that some *cis*- or *trans*-Co(C(5,12)-*rac*-Me_6[14]aneN_4)$(OH_2)_2{}^{3+}$ was present. Assuming the solution contained predominantly the carbonato complex, then [Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3^+] = 6 × 10^{-5} *M*. Therefore K_{sp} = [Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3^+][ClO_4^-] ≃ 4 × 10^{-5} M^2.

The above observations may be used to estimate the stability of Co(C(5,12)-*rac*-Me_6[14]aneN_4)CO_3^+ relative to *cis*-Co(C(5,12)-*rac*-Me_6[14]aneN_4)$(OH_2)_2{}^{3+}$. Thus for

$$CO_2(aq) + \alpha\text{-}cis\text{-}Co(N_4)(OH_2)_2{}^{3+} \overset{K_8}{\rightleftarrows} \alpha\text{-}Co(N_4)CO_3{}^{+} + H_2O + 2H^+ \tag{8}$$

$$K_8 = \frac{[\alpha\text{-}Co(N_4)CO_3{}^+][H^+]^2}{[CO_2(aq)][\alpha\text{-}cis\text{-}Co(N_4)(OH_2)_2{}^{3+}]} = \frac{K_{sp}[H^+]^2}{[ClO_4{}^-][CO_2][\alpha\text{-}cis\text{-}Co(N_4)(OH_2)_2{}^{3+}]}$$

Substituting values of [CO_2] ≅ 3.3 × 10^{-3} *M*,[19] [H^+] =

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[24] Under these conditions the solution would contain a mixture of *cis*- and *trans*-Co$(N_4)(OH_2)_2{}^{3+}$ complexes.[7] The exact distribution of species is unknown although α-*cis*-Co(C(5,12)-*rac*-Me_6[14]aneN_4)$(OH_2)_2{}^{3+}$ appears to comprise about 50% of the mixture;[7] thus K_2 could be of the order of 10^2 *M*.

$[ClO_4^-] = 0.6\ M$, and [α-*cis*-Co(N$_4$)(OH$_2$)$_2^{3+}$] $< 2 \times 10^{-4}\ M$,[24] then $K_8 > 36\ M$.

One would expect Co(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)CO$_3^+$ to become more stable as the [H$^+$] decreases. However the α-*cis*-Co(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)(OH$_2$)$_2^{3+}$ complex is a relatively unstable species and in dilute acid isomerizes to more stable trans complexes ($t_{1/2}$ varies from about 30 min at pH 1 to about 20 sec at pH ~3). In basic solution the initial spectral changes occurred on mixing, and only minor changes of absorbance, presumably due to equilibration among trans isomers, were observable with normal spectrophotometric techniques. Thus we could not observe the equilibration of α-*cis*-Co(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)(OH)$_2^+$ with CO$_3^{2-}$. On the other hand it was possible to observe the reactions of Co^{III}(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)X$_2$ complexes with CO$_3^{2-}$ and HCO$_3^-$.

Since the *trans*-Co(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)(OH)$_2^+$ complexes formed rapidly when α-*cis*-Co(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)(OH$_2$)$_2^{3+}$ was treated with base, we have used solutions of [α-*trans*-Co(5,12)-*rac*-Me$_6$[14]aneN$_4$)-Cl$_2$]ClO$_4$[25] to examine some aspects of the interaction of basic carbonate with Co^{III}(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)-X$_2$ complexes. We found that addition of $1.2 \times 10^{-2}\ M$ Na$_2$CO$_3$ to a solid [α-*trans*-Co(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)-Cl$_2$]ClO$_4$ resulted in the formation of a saturated solution of α-Co(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)CO$_3^+$. However, if [α-*trans*-Co(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)Cl$_2$]ClO$_4$ was first dissolved in water and then treated with basic carbonate, a new more soluble species, RCO$_3$, was formed which had its absorption maximum at 540 nm (ϵ_{max} ~150 M^{-1} cm^{-1}). This species was formed rapidly for $10^{-8}\ M \leqslant [OH^-] \leqslant 0.006\ M$ and must depend on the formation of the more stable (γ, δ, etc.)-*trans*-Co^{III}(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)-XY (XY = Cl$^-$, OH$^-$, or H$_2$O) configurational isomers from α-*trans*-Co^{III}(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)XY.[6,7] First-order plots of the absorbance changes were curved in every case (regardless of [OH$^-$] or [CO$_3^{2-}$], etc.), possibly reflecting variations in the reactivity of the various *trans*-Co(N$_4$)(OH)$_2^+$ isomers. Initial pseudo-first-order rate constants were $(5 \pm 2) \times 10^{-3}$ sec^{-1} ([HCO$_3^-$] $= 6 \times 10^{-3}\ M$, [Co^{III}(N$_4$)X$_2$] $= 2 \times 10^{-3}\ M$; 25°, $\mu = 0.02$) and $(1.6 \pm 0.3) \times 10^{-3}$ sec^{-1} ([CO$_3^{2-}$] $= 5 \times 10^{-3}\ M$, [Co(N$_4$)(OH$_2$)$^+$] $= 2 \times 10^{-3}\ M$; 25°, $\mu = 0.04$). The reaction appeared to generate a distribution of dihydroxy and carbonato complexes.

When equilibrated solutions of basic carbonate and Co(N$_4$)-(OH)$_2^+$ were acidified to pH ~1 (HClO$_4$), the absorbance at 550 nm very slowly decreased (⩽10%/hr). On standing 24 hr [Co(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)CO$_3$]ClO$_4$ precipitated from such solutions; the species remaining in solution had a 562-nm absorption maximum, consistent with Co(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)(OH$_2$)$_2^{3+}$. When equilibrated CO$_3^{2-}$-Co(C(5,12)-*rac*-Me$_6$[14]aneN$_4$)(OH)$_2^+$ solutions were acidified to [H$^+$] $\geqslant 1\ M$, the absorbance decreased rapidly and the resulting solutions contained *trans*-Co(N$_4$)(OH$_2$)$_2^{3+}$ and/or *trans*-Co(N$_4$)ClOH$_2^{2+}$.

E. Observations on Acid Hydrolysis of α-Co(C(5,12)-Me$_6$[14]aneN$_4$)CO$_3^+$. The earlier studies of Kernohan and Endicott[8] were performed on solutions made from the chloride salt of the carbonato complex. Since the hydrolytic reactions appeared to be sensitive to the presence of Cl$^-$ and since more recent work[6,7] has indicated that the *cis*-Co(C(5,12)-Me$_6$[14]aneN$_4$)(OH$_2$)$_2^{3+}$ is more stable than reported in the previous study, we have reinvestigated the acid hydrolysis of this complex. Data in Table V show that the acid hydrolysis rate constant is indeed very sensitive to the anionic composition of the medium. We would estimate that the value of $k' = k_{obsd}/[H^+]$ reported by Kernohan and Endicott was too large by a factor of about 4 at 73.5°. Extrapolation of data in Table V to 25° would give an apparent second-order acid hydrolysis rate constant of $8 \times 10^{-6}\ M^{-1}$ sec^{-1} ($E_a \approx 25$ kcal/mol). The actual value may be less than this.

Table V. Acid Hydrolysis of α-Co(C(5,12)-Me$_6$[14]aneN$_4$)CO$_3^+$ [a]

Temp, °C	[H$^+$], M	X	10^4k_{obsd}, sec^{-1}	$10^3k'$,[b] M^{-1} sec^{-1}
55.0 ± 0.5	0.05[c]	Cl	0.58	1.2
	0.25	Cl	13.8	5.5
	0.25	NO$_3$	1.7	0.69
65.0 ± 0.5	0.125[d]	Cl	10.6	8
	0.25	Cl	46	18
	0.25	NO$_3$	5.5	2.2
	0.125	Cl	17	14
	0.125	Cl, Br[e]	12	10
	0.125	Cl, NO$_3$[f]	8.9	7

[a] Perchlorate salt. Ionic strength = 0.25 (HX + NaX) except as indicated. [b] $k' = k_{obsd}[H^+]$. [c] $\mu = 0.05$. [d] $\mu = 0.125$. [e] 0.125 M NaBr. [f] 0.125 M NaNO$_3$.

F. Mechanistic Considerations for the Tetraamine Complexes. For two of the three isomeric tetramine complexes there is no evidence of significant buildup in concentration of a ring-opened intermediate; for α-Co(C(5,12)-*rac*-Me$_6$-[14]aneN$_4$)CO$_3^+$ the situation is less clear. The initial increase in near-ultraviolet absorptivity observed for the last complex could in principle arise from the intermediate formation of some strongly absorbing, metastable *trans*-dihydroxy species. The buildup of appreciable concentrations of *trans*-hydroxycarbonato complexes should have been detected when partly hydrolyzed solutions were acidified and can therefore be ruled out. Since the tetramine complexes have a demonstrated affinity for carbonate in solutions with pH ⩽12, we infer that the kinetic pecularities (*e.g.*, Figure 7) of stage II arise largely from this reversibility of the carbonate hydrolysis in base and that with [OH$^-$] $< 0.05\ M$, curvature of the pseudo-first-order kinetic plots (Figure 7) was the result of approach to an equilibrium distribution of *trans*-Co(N$_4$)OHCO$_3$ and *trans*-Co(N$_4$)(OH)$_2^+$; K = [Co(N$_4$)OHCO$_3$][OH$^-$]/[Co(N$_4$(OH)$_2^+$][CO$_3^{2-}$] would only have to be greater than about 10 to produce the effect we have observed. For these reasons we believe that the initial part of stage II is representative of the decarboxylation step and may be compared directly to stage II for Co(Me$_6$[14]dieneN$_4$)CO$_3^+$. The similar rate laws for decarboxylation (*i.e.*, stage II) of Co(Me$_6$[14]dieneN$_4$)CO$_3^+$ and the three tetramine complexes are consistent with a similar mechanism for this step; but in such an analysis the key ring-opened intermediate (apparently a trans complex) for the latter complexes could only be present in very low, stationary-state concentrations which are independent of [OH$^-$]. This is not unreasonable, since both formation and decarboxylation of the intermediate are [OH$^-$] dependent. It should also be noted that some of the species formed in basic carbonate solutions of the cobalt(III)-tetramine complexes are too stable in acid to be simply *trans*-Co(N$_4$)OHCO$_3$ complexes; additional side reactions, *e.g.*, dimerization (compare the oxo-bridged dimers investi-

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[25] The configurational isomer which we designate as α-*trans*-Co(C(5, 12)-*rac*-Me$_6$[14]aneN$_4$)Cl$_2^+$ has been elsewhere identified with the VA'A' configurational isomer of Whimp, *et al.*,[6] and contains the unfolded cyclic tetramine with the same configuration of hydrogen atoms at asymmetric centers as the Vf CC ligand in ref 4 above.

gated by Liteplo and Endicott[26]), may also occur in these systems.

The complexity of these systems precludes our establishing a unique mechanism at the present time. The overall pattern outlined above does appear reasonable; *i.e.*, the bidentate carbonato complexes undergo a combination of ring-opening and isomerization reactions, resulting in *trans*-$Co(N_4)OHCO_3$, followed by decarboxylation of this species in a $[OH^-]$-dependent and apparently reversible reaction.

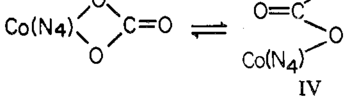
A striking feature of our observations is that *cis*-$Co(N_4)(OH_2)_2{}^{3+}$ can fix CO_2, *i.e.*, that $Co(N_4)CO_3{}^+$ is stable with respect to *cis*-$Co(N_4)(OH_2)_3{}^{3+}$ in mildly acidic solution. By analogy we infer that acidification of a "*cis*-$Co(N_4)OHCO_3$" intermediate is more likely to produce $Co(N_4)CO_3{}^+$ than *cis*-$Co(N_4)(OH_2)_2{}^{3+}$.

General Discussion and Some Comparisons of Mechanism and Stereochemistry. The hydrolysis of the four carbonato complexes described in this study differ in several important ways from previously studied carbonato–amine complexes:[10]

1. Except for the bidentate (*e.g.*, carbonato) complexes, all the known complexes of cis geometry with these cyclic ligands are relatively unstable and have short lifetimes.
2. For the cyclic tetramines the hydrolysis of carbonate is reversible over an extremely large pH range ($1 \geqslant pH \leqslant 10$).
3. The overall hydrolysis rate is greater in 0.1 M OH^- than in 0.1 M H^+.
4. Although Co–O bond breaking was found for acid and base hydrolysis of $Co(N_4)CO_3{}^+$, the intermediacy of a ring-opened intermediate of cis geometry in the base hydrolysis reaction is at best equivocal since there is no evidence for such an intermediate.
5. It is not evident that there is appreciable acid hydrolysis of bidentate carbonate in the tetramine complexes for $[H^+] \leqslant 0.1\,M$ at 25°.

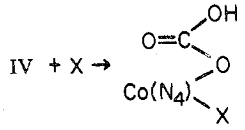
Kernohan and Endicott[8] estimated that the second-order acid hydrolysis rate constant for α-Co(C(5,12)-*rac*-Me_6-[14]$aneN_4$)$CO_3{}^+$ would be $k' \leqslant 10^{-4}\ M^{-1}\ sec^{-1}$ at 25°; from the present study, in Cl^--free solutions, we would estimate that k' is even smaller, less than $10^{-5}\ M^{-1}\ sec^{-1}$ at 25°.

In the present study the ring-opening step appears to be irreversible, and thus steric effects do not have the precise mechanistic significance proposed by Kernohan and Endicott.[8] Furthermore we have demonstrated at least *trans*-$Co(N_4)OHCO_3$ is very rapidly acid hydrolyzed, consistent with the behavior of monodentate carbonate in other complexes.[10-12,17] In view of these observations it seems likely that ring opening in some sense must be the rate-determining step in acid hydrolyses of the present complexes. Our observations lead us to suggest that the steric constraints of the present systems manifest themselves in the formation of a five-coordinate ring-opened complex; *i.e.*, we would visualize ring opening to be a two-step process such as (9) and (10), in which a five-coordinate intermediate is a precursor to the kinetically important ring-opened intermediate. The reaction rate would then depend on ligand stereochemistry insofar as it might affect the lifetime of IV and insofar as it determines the rate constants for trapping IV by various nucleophiles (eq 10). One would expect k_{10} to be greater for $X = Cl^-$ or OH^- than for $X = H_2O$. This analysis is substantially consistent with the data in Table V and with the observed relative rapidity of base hydrolysis.



IV

(9)



(10)

Points 1, 2, and 4 above contrast with the hydrolytic behavior of $Co(en)_2CO_3{}^+$ and are likely manifestations of the complex stereochemistry of the C(5,12)-*rac*-Me_6[14]$aneN_4$ ligand. We feel that points 3 and 5 also result from repulsive interactions attendant on crowding two monodentate ligands into the cis position in these complexes. We agree with Francis and Jordan[27] that the macrocyclic ligand is not likely to "crowd" the chelated carbonate (see also ref 6). In fact the relatively high stability of chelated carbonato and nitrato[16] ligands in C(5,12)-*rac*-Me_6[14]$aneN_4$ complexes must be attributed to the efficient use these ligands make of the available coordination space; the most apparent steric problems enter when these small bidentate ligands are replaced by more space-filling monodentate ligands. Certainly the pK_a correlation attempted by Francis and Jordan[27] is not the single answer to questions of carbonate hydrolysis; in this connection note that the "average" pK_a's of phenanthroline and C(5,12)-*rac*-Me_6[14]$aneN_4$ are in the inverse order of their hydrolytic reactivities at 25° and that since pK_a's contain very substantial contributions from solvation effects, they are not apt to be generally reliable measures of the "electron-donor"[27] capacity of the amine ligands. On the other hand there must be a number of factors which contribute to the reactivities of the diverse group of carbonato-amine-cobalt(III) complexes which have now been examined (see reviews in refs 8-10, 27); electronic effects,[27] carbonate ring strain,[11] and steric effects[8] may each play some role even as they (except carbonate ring strain) contribute to some degree to reactivity patterns in the ligand-exchange reactions of six-coordinate cobalt(III) complexes in general[2,28] or complexes containing cyclic ligands specifically.[12,21,22]

Registry No. $Co(Me_6[14]dieneN_4)CO_3{}^+$, 29224-09-7; α-Co[C(5,12)-*rac*-Me_6[14]$aneN_4$]$CO_3{}^+$, 40273-12-9; β-Co[C-(5,12)-*rac*-Me_6[14]$aneN_4$] $CO_3{}^+$, 40273-13-0; Co[C(5,14)-*meso*-Me_6[14]$aneN_4$] $CO_3{}^+$, 40273-14-1; $Co(Me_6[14]dieneN_4)$-$OHCO_3$, 40273-15-2; {α-*cis*-Co[C(5,12)-*rac*-Me_6[14]$aneN_4$]-$(H_2O)_2$},$^{3+}$, 40354-49-2; CO_2, 124-38-9.

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