Kinetics and Mechanism of Aquation of Carbonato Complexes of Cobalt (III). IV. Influence of Ligand Geometry on the Acid-Catalyzed Hydrolytic Ring-Opening Reactions of Chelated Tetraaminecarbonatocobalt(III) Complex Ions

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Abstract: A study has been made of the aquation reactions of several additional complex ions of the general formula $CoN_4CO_3^+$, where N_4 represents tris-β-aminoethylamine (tren), the α and β configurations of triethylenetetramine (trien), and cis and trans arrangements of the diammineethylenediamine [$(NH_3)_2en$] group of ligands. The reactivity of the tren species is similar to that of the previously reported tetraammine. Some stopped-flow data for the tren complex under high-acidity conditions enable direct confirmation of the existence of the dechelated reactive intermediate $CoN_4(OH_2)(CO_3H)^{2+}$ in the series of reactions constituting the proposed aquation mechanism. Some considerable contrasts appear in the rates of the acid-catalyzed portion of the process, such that at 25° the α-trien species is over a factor of 20 more reactive than its β-trien isomer, and the *trans*-$(NH_3)_2en$ complex is more reactive than its cis analog by a factor of 10. Variations in the ligand geometry seem to offer the most reasonable basis of explanation of the observed contrasts, the factors involved being differences in the strain within the –O–Co–O– linkage of the carbonato chelate, and in the protection of the Co–O bond from attack by H_3O^+ ion. Detailed rate data are tabulated for each of the nine complexes of the type $CoN_4CO_3^+$ for which results are now available in our laboratory, and comparisons are provided with data obtained by other workers for four other complexes in this series. It is now apparent that, depending on the nature of the N_4 amine ligand group, the magnitude of the rate constant for acid-catalyzed aquation at 25° can vary between the limits 10^{-4} and 10 M^{-1} sec^{-1} for this class of carbonatocobalt(III) complex ions.

Our two preceding papers in this series[2,3] reported on the mechanism of the aquation reactions of carbonatocobalt(III) complex ions of the general formula $CoN_4CO_3^+$, where $N_4 = (NH_3)_4$, $(en)_2$, $(pn)_2$, or $(tn)_2$ (en = ethylenediamine, pn = propylenediamine, and tn = trimethylenediamine). In all four cases, the rate-determining step within the acidity range $2 < pH < 5$ is ring opening of the chelated carbonate group, catalyzed both by water and hydronium ion. The proposed mechanism consisted of a combination of these parallel rate-limiting ring-opening processes,[4] a pair of acid–base equilibria, and a rapid decarboxylation, *viz.*

$$\mathrm{CoN_4CO_3^+ + H_2O \longrightarrow \mathit{cis}\text{-}CoN_4(OH)(CO_3H)^+} \qquad k_0 \tag{1}$$

$$\mathrm{CoN_4CO_3^+ + H_3O^+ \longrightarrow \mathit{cis}\text{-}CoN_4(OH_2)(CO_3H)^{2+}} \qquad k_1 \tag{2}$$

$$\mathrm{\mathit{cis}\text{-}CoN_4(OH_2)(CO_3H)^{2+} + H_2O \rightleftharpoons \mathit{cis}\text{-}CoN_4(OH)(CO_3H)^+ + H_3O^+} \qquad K_1 \tag{3}$$

$$\mathrm{\mathit{cis}\text{-}CoN_4(OH_2)_2^{3+} + H_2O \rightleftharpoons \mathit{cis}\text{-}CoN_4(OH)(OH_2)^{2+} + H_3O^+} \qquad K_2 \tag{4}$$

$$\mathrm{\mathit{cis}\text{-}CoN_4(OH_2)(CO_3H)^{2+} \longrightarrow \mathit{cis}\text{-}CoN_4(OH)(OH_2)^{2+} + CO_2} \qquad k_2 \tag{5}$$

The rate law which accurately describes the variation in the magnitude of the observed pseudo-first-order rate constant, k, with the acidity takes the form

$$k = k_0 + k_1[H^+] \tag{6}$$

This rate law can be derived from the mechanism proposed, on the assumption that k_2 greatly exceeds $k_1[H^+]$, which appears to be true down to pH 2 in the tetraammine case,[2] though there is some evidence in runs at higher acidities that the limiting experimental rate constant of $k = k_2$ is approached.

For the four compounds mentioned above, among which the ligand geometry contrasts are not great, the values of k_0 are essentially identical, and the variation in k_1 is relatively small, with only the $(NH_3)_4$ species deviating appreciably from the three bidentate amine species, $(en)_2$, $(pn)_2$, and $(tn)_2$. However, one might expect to observe greater differences in the kinetic parameters when larger contrasts exist in the N_4 ligand arrangement. Such effects have been noted, for example, in the carbonate ligand-exchange rates[6] of the cis and trans forms of the ion $Co(NH_3)_2enCO_3^+$, a pair of compounds in which in the former the ethylenediamine chelate bridge is diagonally placed with respect to the carbonato chelate, while in the latter the two chelate bridges are coplanar. Other types of influence might well be expected in compounds containing multidentate N_4 groupings, such as tren (tris-β-aminoethylamine), trien (triethylenetetramine), etc.

We now report stereochemical effects of considerable magnitude on the rate parameters of the aquation reactions of several $CoN_4CO_3^+$ complex ions of the types just mentioned. Surprisingly, the nonrearrangeable tetradentate amine complex in which N_4 = tren does not differ greatly from the nonchelated tetraammine analog.[7] However, for the tren species k_1 is large

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(2) T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, **91**, 3207 (1969).

(3) V. S. Sastri and G. M. Harris, *ibid.*, **92**, 2943 (1970).

(4) The alternative formulation of the ion *cis*-$CoN_4(OH)(CO_3H)^+$ of reaction 1 is *cis*-$CoN_4(H_2O)(CO_3)^+$, and the choice between these is not unequivocally determinable. The pK of the ion when $N_4 = (en)_2$ is about 8.8 at room temperature [H. Scheiddeger and G. Schwarzenbach, *Chimia*, **19**, 166 (1965)], which is greater than the 8.2 value for *cis*-$Co(en)_2(H_2O)(OH)^{2+}$[5] and much greater than the 6.7 figure for *cis*-$Co(en)_2(H_2O)(C_2O_4)^+$ (where the acidic proton is undoubtedly on H_2O: S. C. Chan and G. M. Harris, unpublished work). On balance, it appears that the coordinated water is a somewhat stronger acid than the monodentate bicarbonate, supporting the structure we have adopted in (1).

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

(6) R. J. Dobbins and G. M. Harris, *J. Amer. Chem. Soc.*, **92**, 5104 (1970).

(7) The mechanism of the aquation of the tren complex is discussed

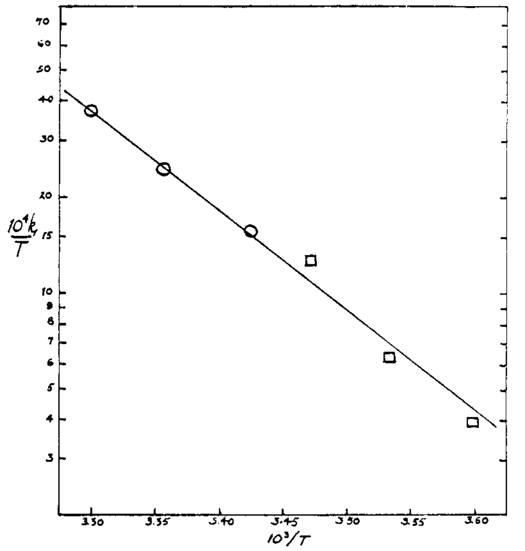

Figure 1. Plot of temperature variation of observed acid-catalyzed aquation rate constant of $Co(en)_2CO_3^+$ complex ion: ○, spectrophotometric data; □, acidometric data.

enough and k_2 small enough that at high acidity the rate of decarboxylation no longer exceeds that of acid-catalyzed ring opening of the carbonate group. This has enabled positive detection of the dechelated bicarbonatoaquo intermediate in stopped-flow experiments, the existence of which could previously only be assumed.[2,3] Substantial contrasts are observed in the aquation behavior of the isomeric forms of $Co(NH_3)_2enCO_3^+$ and of $Co(trien)CO_3^+$, both between the stereoisomeric pairs and with respect to other members of the $CoN_4CO_3^+$ series, effects which appear to be largely explainable in terms of ligand geometry factors.

Experimental Section

Carbonatobis(ethylenediamine)cobalt(III) chloride was prepared by standard procedure[8] and its purity confirmed by spectrophotometric measurements[9] and by analysis.[10] Crude *cis-* and *trans-*$Co(NH_3)_2enCO_3ClO_4$ prepared by R. J. Dobbins[6] were purified by recrystallization from water and the purities checked by spectral comparison with known pure samples.[11] Tris-β-aminoethylamine trihydrochloride was prepared starting from commercially obtainable[12] *N*-(2-bromoethyl)phthalimide. Anhydrous ammonia is passed through the latter in the molten form (140–150°, 6 hr), resulting in its conversion to triphthalimidotriethylamine. This product is hydrolyzed to tren by refluxing with dilute HCl (9 hr). Carbonato(tren)cobalt(III) perchlorate is then obtained by the lead(IV) oxidation procedure[13] and the purity of the compound checked by analysis.[14] *Anal.* Calcd for $Co(tren)CO_3ClO_4 \cdot H_2O$: Co, 15.4; C, 22.0; H, 5.2; N, 14.6. Found: Co, 15.4; C, 21.9; H, 5.3; N, 14.6. The α and β isomers of $Co(trien)CO_3ClO_4 \cdot H_2O$ were prepared as previously described[15] and their purities checked by analysis.[14] *Anal.* Found[16] for the α and β forms, respectively: Co, 15.3 and 15.4; C, 21.9 and 21.9; H, 5.3 and 5.3; N, 14.5 and 14.6. The spectra of the various tetradentate carbonato species were determined on a Cary Model 15 spectrophotometer and agree well with published data.[13,15] The rate-constant data were obtained as already described,[17] using the following wavelength and absorbance values for the spectrophotometric studies

	cis- $(NH_3)_2en$	*trans-* $(NH_3)_2en$	tren	α-trien	β-trien
Peak λ, mμ	500	520	504	503	503
Carbonato absorptivity	125	95	132	124	180
Diaquo absorptivity[18]	82	60	109	90	120

At the lower acidities, pH control was achieved by phosphate-citrate buffering. The ionic strength (usually 0.5 *M*) was established by addition of the requisite amounts of sodium perchlorate. Acidity measurements of the buffered systems were made with a Beckman expanded-scale pH meter, the readings being calibrated such that pH = $-\log[H^+]$.

Results and Discussion

Some acidometric rate-constant measurements were made with the $Co(en)_2CO_3^+$ complex ion in order to supplement and extend the data previously obtained spectrophotometrically.[3] Runs were carried out at 5, 10, and 15° at an ionic strength of 0.5 *M*, in which the initial concentrations of the $(en)_2$ complex and perchloric acid were 0.005 and 0.01 *M*, respectively. The rate constants for acid-catalyzed ring opening, k_1, as derived from these experiments, together with those from earlier spectrophotometric experiments[19] done in buffered solutions of comparable acidity (pH 2.7) and temperatures of 19, 25.1, and 30.1°, are plotted in the conventional manner in Figure 1. It is seen that the two sets of data are completely consistent with one another,[20] as found in the similar comparison for the tetraammine.[2] The rate parameters derived from Figure 1 are $\Delta H^{\ddagger}_1 = 13.8 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger}_1 = -7.4 \pm 3.0$ eu, both values in good agreement with earlier conclusions based on less comprehensive data.[3]

Observations were made of the aquation rates of the ions $Co(tren)CO_3^+$, α- and β-$Co(trien)CO_3^+$, and *cis-* and *trans-*$Co(NH_3)_2enCO_3^+$ by means of the standard spectrophotometric technique (Cary 15 with time-drive chart) in buffered solutions of varying acidities and temperatures at an ionic strength of 0.5 *M*. The results are recorded in Tables I, II, and III and have

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in an abbreviated form in Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J. Sept 1968, No. PHYS 192, and a preliminary report of the stereochemical effect studies is given in *Proc. Int. Conf. Coord. Chem., 12th, 1969*, 12 (1969).

(8) J. S. Holden and G. M. Harris, *J. Amer. Chem. Soc.*, **77**, 1934 (1955).

(9) Close agreement was obtained with the data given in ref 3 for this compound.

(10) Only cobalt was determined, using the $CoSO_4$ method of A. B. Lamb and E. B. Damon, *J. Amer. Chem. Soc.*, **59**, 383 (1937). *Anal.* Calcd for $Co(en)_2CO_3Cl$: Co, 23.2. Found: Co, 22.9.

(11) K. V. Krishnamurty, G. M. Harris, and V. S. Sastri, *Chem. Rev.*, **70**, 171 (1970), Table VII.

(12) Eastman Organic Chemicals, Rochester, N. Y.

(13) H. A. Scheidegger, Doctoral Thesis, Eidgenössischen Technischen Hochschule, Zürich, 1966.

(14) Cobalt was determined by the $CoSO_4$ method (ref 10). C, H, and N analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(15) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967). No attempt was made to separate the possible optical isomers of the α and β species, since it is reasonable to expect that the usual assumption of identity of chemical reactivity applies with respect to the various diastereoisomeric pairs.

(16) The calculated percentages are the same as for the tren analog, since all three tetradentate complexes are monohydrates in the solid state.

(17) Spectrophotometric rate constants were obtained by means of the Cary Model 15 spectrophotometer utilizing the time-drive chart mechanism at the peaks near 500 mμ, or by stopped-flow technique at the higher acidities. Acidometric rate data were obtained by means of a chart-recorded pH-meter setup (see ref 2 for details).

(18) The diaquo complex is readily obtainable *in situ* from the corresponding carbonato species by the addition of slightly more than 2 equiv of perchloric acid. The peak wavelengths are almost identical with those for the corresponding carbonato species given in the table.

(19) These data are recorded in V. S. Sastri, Ph.D. Dissertation, State University of New York at Buffalo, June 1966 (available from University Microfilms, Ann Arbor, Mich.), Appendix 8, p 107.

(20) The Sastri data were obtained at an ionic strength of about 0.2 *M*, as compared to the 0.5 *M* value of the present study. However, as seen in ref 2, Table III, this variation does not have a substantial effect on k_1 and can be ignored in the semilogarithmic temperature variation plot.

been analyzed as before[2,21] to yield values for k_0 and k_1 as presented in Tables IV, V, and VI. Acidometric runs with the tetradentate amine complexes were performed at a number of lower temperatures, and the values of k_1 obtained in this fashion are included in Tables IV and V. A number of stopped-flow runs were made at 25° with the tren complex at acidities up to 2 M (with, of course, an accompanying ionic strength increase) in an attempt to throw further light on the limiting-rate question mentioned in the introduction.

Table I. Spectrophotometric Rate Data (Cary 15 Method) for the Carbonato(tren)cobalt(III) Complex[a]

	Obsd pseudo-first-order rate constant, $sec^{-1} \times 10^3$		
pH	At 15°	At 20°	At 25°
1.5	31.8		
1.6	25.8		
1.75	21.5		
1.8	11.0		
2.0	8.15	9.60	
2.25	4.56		
2.35	3.59		
2.4	4.20	6.23	9.76
2.45	2.88		
2.5	2.90		
2.55	1.89	3.61	6.24
2.7	1.82		
2.75		2.88	
2.8	1.46		3.08
2.95		1.37	
3.0	0.93	1.58	2.04
3.1	0.76	1.20	1.80
3.15	0.69		1.52
3.2	0.61	0.98	1.38
3.3		0.79	1.12
3.35	0.45	0.69	
3.4		0.65	0.93
3.45			0.85
3.5	0.33	0.52	
3.55		0.41	
3.6		0.45	0.65
3.7	0.24	0.40	0.55
3.75		0.39	
3.8			0.50
3.95	0.18		
4.0	0.15		0.40
4.1		0.21	

[a] [Complex ion] = 5×10^{-3} M. Ionic strength = 0.5 M.

The results obtained were as follows (concentration of complex ion 0.005 M in all runs).

($HClO_4$), M	2.00	1.00	0.67	0.49	0.10
Ionic strength, M	2.00	1.00	0.67	0.50	0.50
k, sec^{-1}	1.5	1.4	1.25	1.0	0.3

One notes that the observed rate constant is leveling off to a constant value of about 1.5 sec^{-1} at high acidity, representing a substantial decrease in the second-order rate constant k_1 in this range. Such a decrease cannot reasonably be ascribed to an ionic-strength effect, since an increase of the latter is known[22] to increase k_1, as expected for reaction between ions of the same charge sign. It appears that at 2 M acidity a situation is approached such that k_2 is appreciably smaller than $k_1[H^+]$ and a successive first-order reaction system is set up, *viz.*

$$Co(tren)CO_3^+ + H_3O^+ \xrightarrow{k_1[H^+]} cis\text{-}Co(tren)(OH_2)(CO_3H)^{2+} \xrightarrow{k_2} cis\text{-}Co(tren)(OH)(OH_2)^{2+} + CO_2 \quad (7)$$

This supposition finds credence in the fact that k_1 is known from the accurate lower acidity runs to be 2 M^{-1} sec^{-1}, which means that $k_1[H^+]$ = 4 sec^{-1} in 2 M acid, compared to an expected value[23] of the decarboxylation rate constant k_2 of about 1 sec^{-1}. It is of sig-

Table II. Spectrophotometric Rate Data (Cary 15 Method) for α and β Isomeric Forms of Carbonato(trien)cobalt(III) Complexes[a]

	Obsd pseudo-first-order rate constants, $sec^{-1} \times 10^3$					
	At 20°		At 25°		At 30°	
pH	α	β	α	β	α	β
2.1		1.19		1.33		
2.2		0.77		1.26		1.56
2.25				0.89		
2.3	17.1	0.51				
2.35	13.9		21.6			1.28
2.4	15.6	0.43		0.63	33.5	
2.45		0.40				1.17
2.5			20.5	0.67	26.4	1.05
2.55	8.0	0.31	15.1			
2.6				0.46		0.74
2.65	7.1		12.6		19.3	
2.7				0.43		
2.75			9.4			0.68
2.8	4.8	0.18				0.49
2.85		0.16		0.26	13.3	
2.9	4.1					
2.95				0.21	9.6	
3.0		0.12	5.2			0.30
3.05	3.3			0.18		0.28
3.1	3.1			0.17		
3.15			4.2		6.5	
3.2	2.5	0.08		0.11		0.21
3.25			3.0	0.14		0.18
3.3	1.9			0.09	4.6	
3.35	1.8					
3.4		0.05	2.4	0.08		0.14
3.45				0.075		
3.5	1.3		1.9		3.2	
3.55				0.065		0.12
3.6		0.04	1.5			0.09
3.65	0.84					
3.7		0.03		0.045	1.8	0.07
3.8	0.66	0.22		0.04		
3.85			0.80			0.06
3.9				0.035	1.4	
3.95				0.035		
4.0	0.45	0.02	0.61		1.2	

[a] [Complex ion] = 5×10^{-3} M. Ionic strength = 0.5 M.

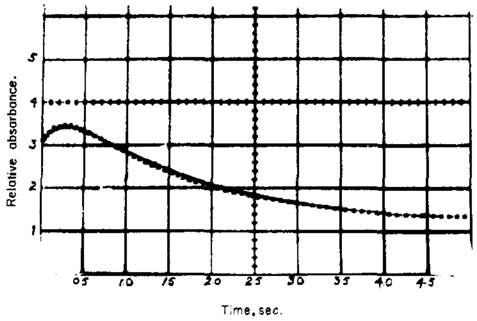

Figure 2. Reproduction of trace obtained in stopped-flow experiment with $Co(tren)CO_3^+$ in 2 M $HClO_4$ at 25°: ordinate, relative absorbance; abscissa, time in seconds. Superposed dotted curve indicates calculated relative absorbance variation with time, as derived in the Appendix.

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[21] The curve fitting was accomplished by the use of a least-squares analysis program with an Olivetti Underwood Programma 101 desk computer.

[22] The increase is small at high ionic strength, but not negligible (see ref 20).

[23] The rate of decarboxylation of the closely similar analog $Co(NH_3)_5CO_3H^{2+}$ is 1.25 sec^{-1} at 25° and 0.5 M ionic strength: T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, **90**, 6360 (1968). See also footnote 26, ref 2.

Table III. Spectrophotometric Rate Data (Cary 15 Method) for Cis and Trans Isomeric Forms of Carbonatodiammineethylenediaminecobalt(III) Complexes^a

	Obsd pseudo-first-order rate constants, sec^{-1} × 10^4					
	At 10°		At 15°		At 20°	
pH	Cis	Trans	Cis	Trans	Cis	Trans
2.25	11.0					
2.3				212		
2.4	8.1	140	13.5		24.2	240
2.45		128				
2.5		120		150	19.0	
2.55			10.0			
2.6	5.0	81				
2.65			7.6			140
2.7	4.0	71			12.5	
2.8	3.2		5.4	82	8.2	110
2.9	2.5	44	4.4	60		84
2.95					6.9	
3.1	1.5	28	2.7	38	4.2	55
3.2	1.3	22	2.1	29	3.7	42
3.3	1.1		1.7		2.9	
3.35				21		
3.4	0.84	14	1.3	19	2.3	27
3.5	0.65		1.1		1.8	
3.55		10		13		20
3.6	0.51	8.6				17
3.7	0.44		0.80	10	1.2	
3.8		5.6				12
3.9	0.28	4.7	0.65	6.7	0.85	

^{a} [Complex ion] = 5×10^{-3} M. Ionic strength = 0.5 M.

Table IV. Summary of Aquation Rate-Constant Data for the Carbonato(tren)cobalt(III) Complex at Ionic Strength = 0.5 M

Temp, °C	10^4k_0, sec^{-1}	k_1, M^{-1} sec^{-1}
5	(0.2)^a	0.5 ± 0.05^c
10	(0.4)^a	0.7 ± 0.05^c
15	0.7 ± 0.04^b	0.87 ± 0.01^b
		1.0 ± 0.1^c
20	1.0 ± 0.2^b	1.4 ± 0.05^b
25	1.7 ± 0.2^b	2.0 ± 0.05^b

^{a} Estimated by use of the derived temperature parameters; see Table VII. ^{b} Obtained from the intercepts and slopes of the k *vs.* [H$^+$] plots of the data given in Table I. ^{c} Values obtained by acidometric technique, each value the mean of three determinations.

Table V. Summary of Aquation Rate-Constant Data for α and β Isomeric Forms of Carbonato(trien)cobalt(III) Complexes at Ionic Strength = 0.5 M

	10^4k_0, sec^{-1}		k_1, M^{-1} sec^{-1}	
Temp, °C	α	β	α	β
10	(0.2)^a	(0.03)^a	1.35 ± 0.05^c	0.035 ± 0.005^c
15	(0.4)^a	(0.06)^a	2.25 ± 0.05^c	0.07 ± 0.01^c
20	0.8 ± 0.4^b	0.08 ± 0.02^b	3.2 ± 0.2^b	0.11 ± 0.01^b
			4.4 ± 0.05^{c,d}	0.10 ± 0.01^c
25	1.5 ± 1.2^b	0.13 ± 0.07^b	5.2 ± 0.1^b	0.18 ± 0.02^b
30	2.7 ± 1.1^b	0.22 ± 0.05^b	8.7 ± 0.1^b	0.29 ± 0.01^b

^{a} Estimated by use of the derived temperature parameters; see Table VII. ^{b} Obtained from the intercepts and slopes of the k *vs.* [H$^+$] plots of the data given in Table II. ^{c} Values obtained by acidometric technique, each value the mean of three determinations. ^{d} Temperature 22° in these runs.

nificance in this regard that the stopped-flow absorbance trace at 2 M acidity indicates an initial *increase* in absorbance followed by a pseudoexponential decay which was used to evaluate the constant k (see Figure 2). This increase is understandable if the absorbance of the ring-opened bicarbonato intermediate (see eq 7) is higher than that of the chelated parent compound. This is in fact known to be the case[24] for the closely related deprotonated species Co(tren)(OH)(CO$_3$) in the 500-mμ region. One can, moreover, calculate[25] the form of the curve of Figure 2 using the rate constants suggested above and absorbance values for the complex species present deduced from the stopped-flow trace. The dotted curve superimposed on this trace in Figure 2 shows how well such a fit can be made, thereby providing substantial support for the concept of the short-lived ring-opened intermediate which previously could only be assumed.

We now turn to consideration of the similarities and contrasts in the rate parameters for aquation of the various CoN$_4$CO$_3^+$ complexes for which results are now available. The rate-constant data are collected in Table VII, together with the corresponding temperature parameters derived from the conventional semilogarithmic plots. The first noteworthy fact is that the k_0 values at 25° are not far from being identical within experimental error, the average value being about 1.1×10^{-4} sec^{-1}. The uncertainty in k_0 arises from the fact that it must be determined from a rather small intercept in a rather large linear extrapolation. The only member of the series which appears to be an exception from the general rule is the β-trien complex with a k_0 of perhaps 10^{-5} sec^{-1}. In this tetradentate, none of the amine bridges is coplanar with the carbonato chelate, in contrast with its α-trien isomer and with the tren analog. It appears that the geometric pattern of the β-trien "wrap-around" enables a reduction in the strain of the O–Co–O coupling of the carbonato chelate, thus inhibiting cleavage of the Co–O bond by water-molecule attack to an extent not possible for any of the other complexes. The temperature parameters governing the magnitude of k_0 are not known accurately enough to form a basis for comment other than that values of about $\Delta H^{\ddagger}_0$ = 17 kcal/mol and $\Delta S^{\ddagger}_0$ = −20 eu describe the situation satisfactorily.

Finally, it is of interest to consider the rate constants k_1 of acid-catalyzed ring opening for the various complexes, among which some considerable contrasts are evident in Table VII. The rate-constant values for the (NH$_3$)$_4$, (en)$_2$, (pn)$_2$, (tn)$_2$, and *cis*-(NH$_3$)$_2$en complexes are all within a factor of 3 of one another, with the mixed-amine ligand species lying between its parent analogs, (NH$_3$)$_4$ and (en)$_2$, as one would expect. The temperature parameters are also in close agreement[26] with mean values of $\Delta H^{\ddagger}_1$ = 16 kcal/mol and

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[24] See ref 13, Figure 9, p 26.

[25] The procedure for this calculation is given in the Appendix to this paper.

[26] The figures for the (pn)$_2$ and (tn)$_2$ complexes are seen to be subject to much larger errors than for the other species, owing to the smaller temperature range over which kinetic measurements were made.

Table VI. Summary of Aquation Rate-Constant Data for Cis and Trans Isomeric Forms of Carbonatodiammineethylenediaminecobalt(III) Complexes at Ionic Strength = 0.5 M[a]

Temp, °C	$10^4 k_0$, sec^{-1}		k_1, M^{-1} sec^{-1}	
	Cis	Trans	Cis	Trans
10	0.06 ± 0.03	0.2 ± 0.1	0.19 ± 0.01	3.5 ± 0.03
15	0.1 ± 0.05	0.4 ± 0.2	0.32 ± 0.01	4.7 ± 0.1
20	0.2 ± 0.1	0.6 ± 0.4	0.53 ± 0.02	6.7 ± 0.2
25[b]	0.3 ± 0.15	1.1 ± 0.6	0.86 ± 0.05	8.9 ± 0.3

[a] Obtained from the intercepts and slopes of the k *vs.* [H$^+$] plots of the data given in Table III. [b] Figures at 25° estimated by use of the temperature parameters derived from the data at the other three temperatures; see Table VII.

Table VII. Rate Parameters for the Aquation Reactions of Various $CoN_4CO_3^+$ Complex Ions at 25° and Ionic Strength = 0.5 M

N_4	$10^4 k_0$, sec^{-1}	$\Delta H^{\ddagger}_0$, kcal/mol	$\Delta S^{\ddagger}_0$, eu	k_1, M^{-1} sec^{-1}	$\Delta H^{\ddagger}_1$, kcal/mol	$\Delta S^{\ddagger}_1$, eu
$(NH_3)_4$[a]	1.3 ± 0.2	12 ± 5	−37 ± 19	1.5 ± 0.1	15.3 ± 1.0	−6.3 ± 3.8
$(en)_2$	1.2 ± 0.2[b]	18 ± 3[b]	−15 ± 9[b]	0.6 ± 0.05[b]	13.8 ± 1.0[c]	−7.4 ± 3.0[c]
$(pn)_2$[b]	1.0 ± 0.2	18 ± 3	−15 ± 9	0.5 ± 0.05	14 ± 3	−13 ± 9
$(tn)_2$[b]	0.8 ± 0.2	16 ± 3	−21 ± 9	0.8 ± 0.05	12 ± 3	−19 ± 9
tren	1.7 ± 0.2	15 ± 2	−25 ± 5	2.0 ± 0.05	11.1 ± 1.0	−20.0 ± 4.0
cis-Diammine	0.3 ± 0.15	17 ± 5	−24 ± 12	0.9 ± 0.05	16.0 ± 1.0	−4.0 ± 3.0
trans-Diammine	1.1 ± 0.6	19 ± 5	−14 ± 12	8.9 ± 0.3	10.0 ± 1.0	−20.0 ± 3.0
α-trien	1.5 ± 1.2	20 ± 3	−7 ± 7	5.2 ± 0.1	15.0 ± 1.0	−5.0 ± 3.0
β-trien	0.1 ± 0.07	17 ± 3	−23 ± 9	0.2 ± 0.02	17.0 ± 1.0	−5.0 ± 3.0
trans-[14]diene[d]				(0.008)	(24[e])	
tet-*b*[d]				(10^{-4})[f]		
$(dipy)_2$[g]				(10^{-4})[h]	(22.3)	(−1.5)
$(phen)_2$[g]				(10^{-4})[h]	(20.4)	(−8.6)

[a] Reference 2, Table II. [b] Reference 3, Table I. [c] Deduced from straight-line fit to temperature-dependence data (Figure 1). [d] A. J. Kernohan and J. F. Endicott, *J. Amer. Chem. Soc.*, **91**, 6977 (1969), Table II. [e] Reported in ref *d* as an Arrhenius activation energy, E_a = 24.3 kcal/mol. [f] Extrapolated from data at 73.5° assuming same heat of activation as for *trans*-[14]diene. [g] R. B. Jordan, Department of Chemistry, University of Alberta, Canada, private communication, 1970. [h] Estimated by use of the reported temperature parameters, obtained in the range 50° < t < 71°.

$\Delta S^{\ddagger}_1$ = −6 eu for these five complexes. The tren analog has a k_1 value at 25° not far from the five aforementioned, but its temperature parameters differ appreciably, with the lower enthalpy of activation possibly related to the increased strain of the O–Co–O linkage due to the coplanar amine–carbonato bridging alluded to earlier, but with this effect largely canceled out by a more negative entropy of activation. Substantial deviations from the pattern are seen for the *trans*-$(NH_3)_2$en complex, with a k_1 value at 25° greater by a factor of 10 than that of its *cis* isomer, and for α-trien, with its k_1 greater than for the β-trien isomer by a factor of 26. The contrasts between the trans and cis pair and between the α and β pair are attributable to the contrast between coplanar and diagonal orientations of amine and carbonato chelates, with hydronium ion attack on the Co–O linkage according to reaction 2 facilitated by the greater carbonato chelate ring strain in the coplanar species and marked by a lowered enthalpy of activation, as with the tren complex. The β-trien complex has an unusually small k_1 value, even for a species with diagonal orientation of chelates, so other factors must contribute. In this case the carbonato oxygens attached to cobalt are possibly somewhat protected from H_3O^+ attack by the wrap-around character of the tetradentate amine chelate. One might expect, therefore, that tetradentate amines offering more stereochemical hindrance would have even greater retarding influence on the acid-catalyzed ring-opening process. This expectation is confirmed by some recent data[27] on the rate of this reaction for the carbonatocobalt(III) species in which N_4 is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (*trans*-[14]diene) or 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet-*b*). As seen in Table VII, the first of these has a k_1 value only $^1/_{25}$th as great as that for our slowest analog, β-trien, while the tet-*b* complex has a k_1 smaller than this by another factor of about $^1/_{100}$. Additional data of this kind are now available[28] for the complex ions in which N_4 is bis(dipyridyl) or bis(phenanthroline), where the k_1 values (see Table VII) are apparently as low as for tet-*b*. Clearly, one is achieving an unusual degree of protection of carbonate ion from its reaction with 1 M acid when its half-time for decarboxylation in such a medium at room temperature is approaching 2 hr!

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Appendix

For the successive first-order reaction system

$$X \xrightarrow{k_x} Y \xrightarrow{k_y} Z$$

in which only reactant X is initially present, the mole fractions of the various species present at time t are given by

$$f_x = e^{-k_x t}$$

$$f_y = \frac{k_x}{k_x - k_y}(e^{-k_y t} - e^{-k_x t})$$

$$f_z = 1 - f_x - f_y$$

If the relative absorbances of X, Y, and Z are given by A_x, A_y, and A_z, the total relative absorbance of the system at any time t is expressed by

$$T = A_x f_x + A_y f_y + A_z f_z \qquad (8)$$

In the present system, $k_x = k_1[H^+] = 4$ sec^{-1} and $k_y = k_2 = 1$ sec^{-1}. A_x and A_z may be read off from the plot (Figure 2) as the relative absorbances at times $t = 0$ and $t = \infty$, respectively, and are seen to have the values 3.0 and 1.4, respectively. The curve is fitted by assigning A_y the reasonable value of 4.2. The dotted curve superimposed in Figure 2 is then calculated by the use of eq 8.

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

(28) R. B. Jordan, Department of Chemistry, University of Alberta, Canada, private communication, 1970.