Kinetics and Mechanism of the Hydrolysis of *cis*-β-Carbonato(3,7-diazanonane-1,9-diamine)cobalt(III) and *cis*-β-Carbonato(4,7-diazadecane-1,10-diamine)cobalt(III) Cations in Acidic Aqueous Solution

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The acid-catalysed hydrolyses of the complex cations *cis*-β-[CoL(CO$_3$)]$^+$ [L = 3,7-diazanonane-1,9-diamine (L^1) or 4,7-diazadecane-1,10-diamine (L^2)] have been studied over the ranges $30.0 \leqslant \theta \leqslant 40.0$ °C and $1 \leqslant pH \leqslant 5$ (for L^2, $1 \leqslant pH \leqslant 2$) at an ionic strength of 0.5 mol dm^{-3}. The kinetic results exhibit a rate law of the form $-d(\ln [\text{complex}])/dt = k_0 + k_1[H^+]$ where the values of k_0 (25 °C), k_1 (25 °C), $\Delta H^\ddagger_0$, $\Delta S^\ddagger_0$, $\Delta H^\ddagger_1$, and $\Delta S^\ddagger_1$ are 1.0×10^{-4} s^{-1}, 0.17 dm^3 mol^{-1} s^{-1}, 95 ± 15 kJ mol^{-1}, −4 ± 4 J K^{-1} mol^{-1}, 37 ± 2 kJ mol^{-1}, and −137 ± 20 J K^{-1} mol^{-1} for the L^1 complex and 3.9×10^{-5} s^{-1}, 2.7×10^{-2} dm^3 mol^{-1} s^{-1}, 72 ± 10 kJ mol^{-1}, −84 ± 25 J K^{-1} mol^{-1}, 72 ± 4 kJ mol^{-1}, and −34 ± 8 J K^{-1} mol^{-1} for the L^2 complex. The acid-catalysed reactions are subject to a deuterium solvent isotope effect, consistent with a mechanism involving a rapid protonation equilibrium followed by slow ring opening of the carbonate ring. The diaqua product of the acid hydrolysis of the L^2 complex undergoes *cis*-to-*trans* isomerization at rates comparable to the hydrolysis reaction under certain conditions. The values of k_{iso} at 25 °C (I = 0.5 mol dm^{-3} HClO$_4$) and corresponding activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, are 1.1 ± 0.05 s^{-1}, 115.8 ± 2.5 kJ mol^{-1}, and 67 ± 21 J K^{-1} mol^{-1} respectively.

The reactivity of co-ordinated carbonate ligands has been the subject of vigorous research in recent years.[1] Of particular interest is the aquation of cobalt(III) complexes of general formula [CoN$_4$(CO$_3$)]$^+$ where N$_4$ stands for any combination of uni-, bi-, tri-, and quadri-dentate amine ligands. The mechanism which has now been generally accepted[2–4] consists of ring opening of the chelated carbonate group catalysed both by water and by oxonium ion, followed by a decarboxylation of the unidentate intermediate as shown in equations (1)—(5).

$$[CoN_4(CO_3)]^+ + H_2O \xrightarrow{k_0} [CoN_4(OH_2)(CO_3)]^+ \quad (1)$$

$$[CoN_4(CO_3)]^+ + H_3O^+ \xrightarrow{k_1} [CoN_4(OH_2)(HCO_3)]^{2+} \quad (2)$$

$$[CoN_4(OH_2)(CO_3)]^+ + H_3O^+ \xrightleftharpoons{K_1} [CoN_4(OH_2)(HCO_3)]^{2+} + H_2O \quad (3)$$

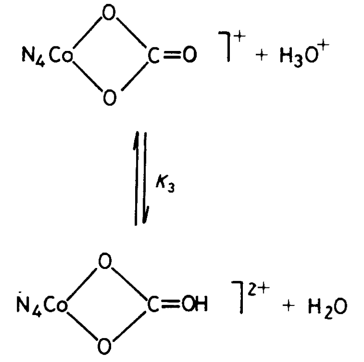
$$[CoN_4(OH_2)(HCO_3)]^{2+} \xrightarrow{k_2} [CoN_4(OH_2)(OH)]^{2+} + CO_2 \quad (4)$$

$$[CoN_4(OH_2)(OH)]^{2+} + H_3O^+ \xrightleftharpoons{K_2} [CoN_4(OH_2)_2]^{3+} + H_2O \quad (5)$$

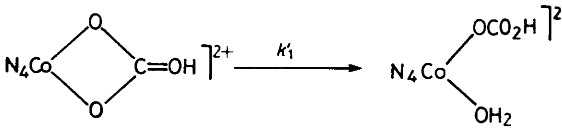
The rate equation (6) describes the variation of the pseudo-first-order rate constants with acidity.

$$k_{obs.} = k_0 + k_1[H^+] \quad (6)$$

However, the acid-catalysed reactions are subject to a deuterium solvent isotope effect[5,6] consistent with a mechanism involving rapid pre-equilibrium protonation followed by a slow ring-opening reaction as in equations (7) and (8). Hence, equation (6) is modified to (9),



(7)



(8)

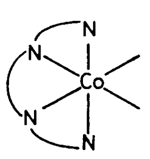
$$k_{obs.} = \frac{k_0 + k'_1K_3[H^+]}{1 + K_3[H^+]} \quad (9)$$

which can be further simplified to (10). Since plots of $k_{obs.}$ *vs.*

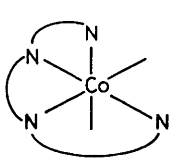
$$k_{obs.} = k_0 + k'_1K_3[H^+] \quad (10)$$

[H$^+$] have been found to be linear for a wide variety of complexes, $K_3[H^+] \ll 1$ has been assumed.[5] Hence k_1 is replaced by k'_1K_3. It was also shown[6] that the values of k_1 or k'_1K_3 vary within six orders of magnitude. This enormous variation has been explained in terms of acid–base properties and the stereochemical influence of the non-participating ligands.

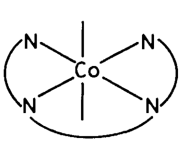
The choice of long-chain linear tetramines as the non-labile ligand in our present study was dictated by the intrinsic interest



cis − α



cis − β



trans

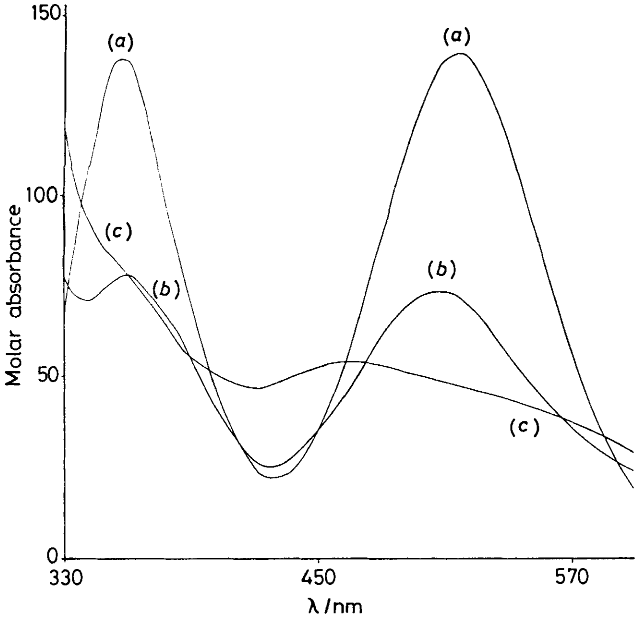


Figure 1. Visible spectra of *cis*-β-$[CoL^2(CO_3)]^+$ (*a*), *cis*-β-$[CoL^2(OH_2)_2]^{3+}$ (*b*), and *trans*-β-$[CoL^2(OH_2)_2]^{3+}$ (*c*)

in linear and cyclic ligands due to the stereochemistry inherent in these octahedral complexes. In these complexes the ligand may adopt any of three geometrical structures as shown. It would be interesting to monitor any geometrical rearrangement in the molecule during and after hydrolytic cleavage of the carbonate ligand. We report here the detailed picture of the rearrangement of the quadridentate ligands and their influences on the rates of ring opening of chelated carbonate.

Results and Discussion

The spectra of the reactant, $[CoL^1(CO_3)]^+$ (L^1 = 3,7-diazanonane-1,9-diamine), and the acid-hydrolysed product, $[CoL^1(OH_2)]^{3+}$ show two absorption bands at round 500 and 360 nm (${}^1T_{1g} \longleftarrow {}^1A_{1g}$ and ${}^1T_{2g} \longleftarrow {}^1A_{1g}$ transitions) characteristic of *cis*-complexes. Comparing these spectra with that of known trien (triethylenetetramine, 3,6-diazaoctane-1,8-diamine) complexes[7] it is concluded* that both reactant and product complexes are in the *cis*-β-configuration. The purity of the isomer has also been confirmed by thin-layer chromatography, i.r. and n.m.r. spectroscopy. It is also to be noted that no *cis*-α form has yet been reported for L^1 complexes and it has been asserted[8] that this form does not exist.

The visible spectra of $[CoL^2(CO_3)]^+$, *cis*-$[CoL^2(OH_2)_2]^{3+}$, which is the immediate product of the acid-catalysed hydrolysis, and *trans*-$[CoL^2(OH_2)_2]^{3+}$ (L^2 = 4,7-diazadecane-1,10-diamine), the final product, are shown in Figure 1. The configuration of $[CoL^2(CO_3)]^+$ has also been assigned as *cis*-β for the same reasons as in the case of the L^1 complex. However, the product of the acid hydrolysis of the former complex shows splitting of the band around 500 nm (${}^1E_g \longleftarrow {}^1A_{1g}$ and ${}^1A_{1g} \longleftarrow {}^1A_{1g}$ transitions) leading us to believe that the product $[CoL^2(OH_2)_2]^{3+}$ is in the *trans* configuration.[9–11]

Pseudo-first-order rate constants for the acid hydrolysis of *cis*-β-$[CoL^1(CO_3)]^+$ over the ranges $1 \leqslant pH \leqslant 5$ and $30 \leqslant \theta \leqslant 40$ °C are presented in Table 1. The rate constants were found to increase with increasing acidity and plots of $k_{obs.}$ *vs.* $[H^+]$ are linear with small positive intercepts. The rate expression, therefore, definitely takes the form of equation (6) and the results can be interpreted satisfactorily in terms of the mechanism depicted in equations (1)—(5). Linear regression analysis of the data in Table 1 yields values of k_0 and k_1 which are presented in Table 3.

In order to obtain support for the mechanism depicted in equations (7) and (8) some experiments were performed in D_2O as solvent in the acidity range 0.01—0.1 mol dm^{-3} (Table 1). This enables us to calculate the overall ring-opening rate in D_2O (Table 3). The value of 2.14 obtained for the ratio of the ring-opening rates in D_2O and H_2O clearly supports the equilibrium mechanism described earlier.[5,6]

The effect of ionic strength on the ring opening rate for *cis*-β-$[CoL^1(CO_3)]^+$ has also been investigated and the data are presented in Table 4. The increase in the rate constants with an increase in ionic strength clearly indicates that two unipositive ions are involved in the rate-determining step.[12]

The effect of temperature on the rate of acid hydrolysis is shown in Table 3 and the activation parameters, $\Delta H^‡$ and $\Delta S^‡$, derived by least-squares analysis of the data in Table 3 using the Eyring–Polanyi equation,[13] are also presented in Table 3.

As discussed before the product of aquation of *cis*-β-$[CoL^2(CO_3)]^+$ is *trans*-$[CoL^2(OH_2)_2]^{3+}$. It is obvious, therefore, that the isomerization is concomitant with the hydrolysis. Since the acid hydrolysis of the carbonato complex is generally[1] a second-order process it was possible to measure the spectrum of the hydrolytic product *cis*-β-$[CoL^2(OH_2)_2]^{3+}$ by adding 4 mol dm^{-3} $HClO_4$ to a 2×10^{-3} mol portion of *cis*-β-$[CoL^2(CO_3)]^+$ at 5 °C. The spectrum of the immediate product as shown in Figure 1 is similar to those of other *cis*-diaqua products[2–4] but completely different from that of the final *trans*-diaqua isomerization product. The acid hydrolysis was, therefore, followed at 360 nm† where the *cis* and *trans* species absorb equally and the rates of isomerization were studied at 450 nm† where there is no interference from the hydrolytic process.

The pseudo-first-order rate constants for the acid hydrolysis of *cis*-β-$[CoL^2(CO_3)]^+$ over the ranges $0.01 \leqslant [H^+] \leqslant 0.1$ mol dm^{-3} and $30 \leqslant \theta \leqslant 40$ °C are presented in Table 2. The effect of $[H^+]$ on the rate constants is the same as in the case of *cis*-β-$[CoL^1(CO_3)]^+$. The plots of $k_{obs.}$ *vs.* $[H^+]$ are linear with small positive intercepts. The rate expression obviously takes the form of equation (10) and hence linear regression analysis of the data in Table 2 yields the values of k_0 and k_1 which are presented in Table 3 along with the activation parameters. It

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* The *cis* isomer usually displays a pronounced shoulder at around 650 nm which has been attributed to a partial splitting of the *A.B.B* $\longleftarrow {}^1A_1$ level.

† The molar absorbance for *cis*-β-$[CoL^2(CO_3)]^+$ at 360 nm was found to be 130 dm^3 mol^{-1} cm^{-1} in good agreement with a literature value[14] of 125 dm^3 mol^{-1} cm^{-1} at the same wavelength. At 450 nm the molar absorbances of *cis*-β-$[CoL^2(OH_2)_2]^{3+}$ and *trans*-$[CoL^2(OH_2)_2]^{3+}$ were found to be 25.5 and 45.6 dm^3 mol^{-1} cm^{-1}.

Table 1. Values of $k_{obs.}$ for the acid-catalysed hydrolysis of *cis*-β-$[CoL^1(CO_3)]^+$ (2×10^{-3} mol dm^{-3}) at $I = 0.5$ mol dm^{-3}

30 °C		35 °C		40 °C	
$[H^+]^a$/mol dm^{-3}	$10^3k_{obs.}$/s^{-1}	$[H^+]$/mol dm^{-3}	$10^3k_{obs.}$/s^{-1}	$[H^+]$/mol dm^{-3}	$10^3k_{obs.}$/s^{-1}
3.02×10^{-6}	0.11	1.95×10^{-5}	0.05	1.38×10^{-5}	0.09
1.29×10^{-5}	0.05	6.76×10^{-5}	0.07	5.25×10^{-5}	0.13
4.90×10^{-5}	0.03	2.40×10^{-4}	0.15	2.04×10^{-4}	0.29
2.90×10^{-4}	0.12	4.07×10^{-4}	0.35	4.90×10^{-4}	0.50
5.37×10^{-4}	0.24	8.71×10^{-4}	0.54	1.59×10^{-4}	0.74
7.59×10^{-4}	0.38	1.95×10^{-3}	0.71	1.12×10^{-3}	1.51
1.38×10^{-3}	0.54	2.69×10^{-3}	1.57	2.29×10^{-3}	2.28
2.40×10^{-3}	0.81	5.37×10^{-3}	2.27	5.31×10^{-3}	3.14
4.37×10^{-3}	1.06	0.01	3.47, 5.87^b	0.01	4.80
0.01	2.52	0.02	6.38, 12.1^b	0.02	7.24
0.02	3.98	0.03	10.1, 18.6^b	0.03	11.1
0.03	6.88	0.04	10.8, 24.1^b	0.04	14.3
0.04	8.95	0.05	14.2, 29.7^b	0.05	18.2
0.05	11.2	0.06	18.7, 35.4^b	0.06	21.9
0.06	12.8	0.07	21.3, 42.5^b	0.07	25.5
0.07	15.0	0.08	26.5, 48.3^b	0.08	29.0
0.08	17.6	0.09	28.1, 54.2^b	0.09	31.9
0.09	19.3	0.10	30.9, 58.8^b	0.10	36.4
0.10	20.8				

[a] The values of $[H^+]$ less than 0.01 mol dm^{-3} were calculated from the measured pH. [b] Measured in D_2O.

Table 2. Values of $k_{obs.}$ for the acid-catalysed hydrolysis of *cis*-β-$[CoL^2(CO_3)]^+$ (2×10^{-3} mol dm^{-3}) at $I = 0.5$ mol dm^{-3}

	$10^3\ k_{obs.}$/s^{-1}		
$[H^+]$/mol dm^{-3}	30	35	40 °C
0.01	0.47	0.75, 1.78	1.30
0.02	0.84	1.41, 2.82	2.24
0.03	1.28	2.81, 4.33	3.63
0.04	1.67	2.87, 5.68	4.75
0.05	2.08	3.52, 7.28	5.88
0.06	2.47	4.31, 8.83	6.67
0.07	3.11	4.78, 10.3	8.06
0.08	3.49	5.67, 11.2	9.50
0.09	3.95	6.44, 12.6	10.2
0.10	4.36	7.22, 14.1	11.62

* Second values measured in D_2O.

was not possible to do measurements at high pH values (> 2), since all available buffers between pH 2 and 5 react with the complex. The deuterium solvent effect in the range $0.01 \leqslant [H^+] \leqslant 0.1$ mol dm^{-3} again provides strong support for the mechanism depicted in equations (7) and (8). The values of k_0 and k_1 in D_2O at 35 °C are also listed in Table 3 and hence it can be calculated that the ratio of the k_1 values in D_2O and in H_2O is 1.98 compared to 2.14 obtained for the corresponding L^1 complex.

Table 4. Effect of ionic strength on the acid-catalysed hydrolysis of *cis*-β-$[CoL^1(CO_3)]^+$ and *cis*-β-$[CoL^2(CO_3)]^+$ (2×10^{-3} mol dm^{-3}) at $[H^+ = 0.01$ mol dm^{-3} and 35 °C

	$10^3\ k_{obs.}$/s^{-1}	
I/mol dm^{-3}	L^1	L^2
0.01	1.16	3.9
0.05	1.28	4.8
0.10	1.43	5.1
0.20	1.48	5.8
0.30	1.54	7.1
0.40	1.58	6.9
0.50	1.59	7.5

The effect of ionic strength on the ring-opening rate of *cis*-β-$[CoL^2(CO_3)]^+$ is also shown in Table 4 and again there is an increase in the rate constants as the ionic strength increases. This observation is in complete agreement with the general mechanistic scheme proposed earlier.

The first-order rate constants for the isomerization of *cis*-β-$[CoL^2(OH_2)_2]^{3+}$ to the corresponding *trans* species are 2.56×10^{-4}, 4.15×10^{-4}, and 11.5×10^{-4} s^{-1} at 30, 35, and 40 °C respectively and at an ionic strength of 0.5 mol dm^{-3}. These rate constants are the average values from at least five runs. The isomerization reactions were studied at 0.5 mol dm^{-3} $HClO_4$. At this concentration of acid the rate of acid hydrolysis

Table 3. Kinetic parameters for acid-catalysed hydrolysis of *cis*-β-$[CoL^1(CO_3)]^+$ and *cis*-β-$[CoL^2(CO_3)]^+$ at $I = 0.5$ mol dm$^{-3\,a}$

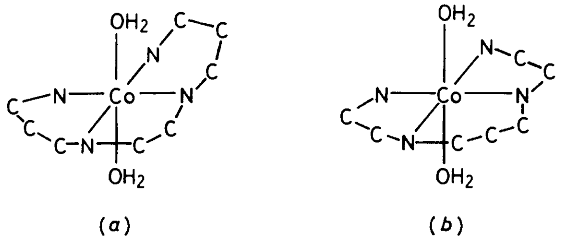
	L^1 complex		L^2 complex	
Templ./°C	10^4k_0	$10^3\ k_1$	$10^4\ k_0$	$10^3\ k_1$
30.0	1.8 ± 0.7	215 ± 1	0.6 ± 0.4	44.2 ± 0.6
35.0	4.3 ± 1.5	277 ± 3	1.0 ± 0.2	70.0 ± 3.0
	3.0 ± 3.0^b	594 ± 6^b	2.6 ± 1.0^b	139.0 ± 4.0^b
40.0	6.2 ± 1.5	353 ± 3	1.7 ± 0.9	114.0 ± 1.0
	$\Delta H_0^\ddagger = 95 \pm 15$	$\Delta H_1^\ddagger = 37 \pm 2.1$	$\Delta H_0^\ddagger = 72 \pm 10$	$\Delta H_1^\ddagger = 72 \pm 4.2$
	$\Delta S_0^\ddagger = -4 \pm 4$	$\Delta S_1^\ddagger = 137 \pm 20$	$\Delta S_0^\ddagger = -84 \pm 25$	$\Delta S_1^\ddagger = -34 \pm 8$

[a] Units: k_0, s^{-1}; k_1, dm^3 mol^{-1}; $\Delta H^\ddagger$, kJ mol^{-1}; $\Delta S^\ddagger$, J K^{-1} mol^{-1}. [b] Measured in D_2O.

Table 5. Rates and activation parameters for the ring-opening reactions of some carbonatocobalt(III) complexes at 25 °C and $I = 0.5$ mol dm^{-3}

Complex[a]	$10^4\,k_0$/s^{-1}	$\Delta H_0^{\ddagger}$/kJ mol^{-1}	$\Delta S_0^{\ddagger}$/J K^{-1} mol^{-1}	k_1/dm^3 mol^{-1} s^{-1}	$\Delta H_1^{\ddagger}$/kJ mol^{-1}	$\Delta S_1^{\ddagger}$/J K^{-1}mol^{-1}	Ref.
$[Co(NH_3)_4(CO_3)]^+$	1.3	50	−155	1.5	64	−26	3
$[Co(en)_2(CO_3)]^+$	1.2	75	−63	0.6	59	−54	4
$[Co(tn)_2(CO_3)]^+$	0.8	67	−88	0.8	50	−79	4
$[Co(pn)_2(CO_3)]^+$	1.0	75	−63	0.5	59	−54	4
α-$[Co(trien)(CO_3)]^+$	1.5	84	−29	5.2	63	−21	4
β-$[Co(trien)(CO_3)]^+$	0.1	71	−96	0.2	71	−21	4
$[Co(tren)(CO_3)]^+$	1.7	63	−105	2.0	46	−89	4
cis-$[Co(en)(NH_3)(CO_3)]^+$	0.3	71	−100	0.9	67	−17	3
β-$[CoL^1(CO_3)]^+$	1.0[b]	95	−4	0.17[b]	37	−137	This work
β-$[CoL^2(CO_3)]^+$	0.4[b]	72	−84	0.03[b]	72	−34	This work

[a] en = $H_2N(CH_2)_2NH_2$, tn = $H_2N(CH_2)_3NH_2$, pn = $H_2NCH_2C(NH_2)CH_3$, and tren = $N(CH_2CH_2NH_2)_3$. [b] Extrapolated from the temperature dependences of k_0 and k_1, and the activation parameters.



(*a*) (*b*)

Figure 2. Structures of (*a*) *trans*-$[CoL^2(OH_2)_2]^{3+}$ showing the 6,5,6-ring system and (*b*) of *trans*-$[CoL^1(OH_2)_2]^{3+}$ showing the 5,6,5-ring system

is too fast ($k_{obs.} = 3.5 \times 10^{-2}$ s^{-1}) to compete with the isomerization rate and also the possibility of interference due to the isomerization of hydroxoaqua species is minimal. The values of $\mathrm{A}H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the isomerization reaction were calculated by linear regression analysis as 115.8 ± 2.5 kJ mol^{-1} and 67 ± 21 J K^{-1} mol^{-1} respectively.

The factors influencing the magnitude of rate and activation parameters for the acid hydrolysis of carbonato complexes in general have been extensively discussed.[1–4,15–18] Those usually considered are solvation, electronic, and steric effects. The values of the ring-opening rate constants and the corresponding activation parameters for an extensive number of carbonato complexes have been summarized elsewhere.[1] Kinetic data obtained for *cis*-β-$[CoL^1(CO_3)]^+$ and *cis*-β-$[CoL^2(CO_3)]^+$ with those of complexes closely related in structure and stereochemistry only are compared in Table 5. One immediately notices that the rate constants for both water-catalysed and oxonium ion-catalysed processes are very similar in their magnitude differing systematically in their activation parameters. This again emphasizes that the factors[4,18] like solvation, electronic, and steric effects are responsible for the differences.

Finally, some comments need to be made on the behaviour of *cis*-β-$[CoL^1(OH_2)_2]^{3+}$ and *cis*-β-$[CoL^2(OH_2)_2]^{3+}$ in terms of their *cis*-to-*trans* isomerization. A plausible reason for the *cis*-β-to-*trans* isomerization of the latter complex in contrast to the former which does not isomerize at all is the comparatively greater stability of a planar system with six-, five-, and six-membered rings as in *trans*-$[CoL^2(OH_2)_2]^{3+}$ over that of a planar system with five-, six-, five-membered rings as in *trans*-$[CoL^1(OH_2)_2]^{3+}$ (Figure 2). This is no doubt essentially due to steric factors probably arising from the greater length and flexibility of the ligand L^2. It was also proposed by Hamilton and Alexander[19] that the nature of the alkyl residues bridging the N atoms in the ligand rather than their linear or macrocyclic character determines the stereochemistry of tetramine ligands around the central cobalt atom. This also explains the unique ability of the diaqua(1,4,8,11-tetra-azacyclotetradecane)-cobalt(III) complex ion to form both *cis* and *trans* isomers.

Experimental

Materials.—All chemicals used were reagent grade. Deionized water, obtained by passing distilled water through a Milli-Q ion-exchange train (Millipore Corporation, Bedford, Massachusetts) or through a Zerolite DM-F mixed resin (BDH Chemicals, England), was used to make up all solutions used for the kinetic and spectral investigations. Deionized water used in the preparations of the buffer solutions was boiled and deaerated with nitrogen.

Synthesis of Ligands and Complexes.—Both ligands L^1 and L^2 were prepared as described by van Alphen.[20]

trans-$[CoL^1Cl_2]ClO_4$. The complex *trans*-$[CoL^1Cl_2]Cl$ was prepared by the method outlined by Hamilton and Alexander[14] starting from $CoCl_2{\cdot}6H_2O$. A sample of the chloride salt (12.4 g) was dissolved in the minimum amount of cold water and $NaClO_4$ (6 g) was added. The green precipitate which formed was filtered off, washed with cold water, and air-dried. Yield 12.1 g.

cis-β-$[CoL^1(CO_3)]ClO_4$. The *trans* perchlorate salt (10 g) was slurried in methanol–water (1:1, 240 cm^3) and then Ag_2CO_3 (7 g) was added. The mixture was heated on a steam-bath for 45 min. A reddish solution was obtained and the AgCl formed was filtered off. Methanol was then removed by vacuum distilation and the solution was freeze-dried. The red solid was repeatedly recrystallized from water–dioxane to give the pure carbonato complex. Yield, 2.2 g (Found:* C, 25.20; H, 5.35; N, 14.95. Calc. for $C_8H_{20}ClCoN_4O_7$: C, 25.40; H, 5.30; N, 14.80%).

cis-β-$[CoL^2(CO_3)]ClO_4$. This complex was prepared by the method of Hamilton and Alexander.[14] The purple-red crystals obtained were recrystallized several times from water–methanol and dried overnight in vacuum at 50 °C. Yield = 0.7 g (Found: C, 27.95; H, 5.60; N, 14.10. Calc. for $C_9H_{22}ClCoN_4O_7$: C, 27.50; H, 5.65; N, 14.25%).

The complex ions $[CoL^1(OH_2)_2]^{3+}$ and $[CoL^2(OH_2)_2]^{3+}$ were produced in solution by treating the corresponding carbonato complexes with 0.1 mol dm^{-3} $HClO_4$ solution. Attempts to isolate the diaqua complexes resulted in very hygroscopic semi-solid materials.

Spectral Studies.—Infrared spectra were taken with a Perkin-Elmer 735B or Pye Unicam SP3-300 spectrophotometer using

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* Elemental analysis was carried out by Mikroanalytiches Labor Pasher, An der Pulvermutile 3, D-5480 Remagen-Bandorf, West Germany.

KBr discs, and visible spectra with a Varian-Cary 219 or Pye-Unicam SP8-100 spectrophotometer.

Kinetic Studies.—Solutions of $HClO_4$ and $LiClO_4$ for the kinetic runs were standardized by known methods.[21] Standard phosphate–citrate buffers[22] were used to stabilize the pH of the solutions for kinetic measurements in the range $2 < pH < 5$. The contribution of the buffer to the total ionic strength was corrected according to the published data.[23]

The kinetic measurements were carried out by using either the Cary 219 spectrophotometer fitted with a Precision Circulation water-bath or the Pye-Unicam SP8-100 UV recording spectrophotometer fitted with a Haake KT33 water-bath. The temperature in the cell compartments was monitored by a digital Cole Parmer 8502-20 thermometer and the pH of the reactant solutions was measured with a Beckman model 3500 digital pH meter fitted with a Cole Parmer pH electrode positioned in the thermostatted solution in the cell compartment of the spectrophotometer; 10-mm and 20-mm quartz cells were used. Standard phthalate (pH 4.008 at 25 °C) and phosphate (pH 6.865 at 25 °C) buffer solutions thermostatted in the cell compartments of the spectrophotometer were used to calibrate the pH meter. Rate constants were calculated from data obtained by repetitive scanning and by time-drive chart spectroscopy between pH 1 and 5 and $30.0 < \theta < 40$ °C. Time-drive chart spectroscopy was performed at 510 nm for the hydrolysis of *cis*-β-$[CoL^1(CO_3)]ClO_4$.

In a typical experiment, a weighed amount of the complex equivalent to 2×10^{-3} mol was quickly dissolved in a 5-cm^3 (20-mm cell) or 2.5-cm^3 (10-mm cell) portion of $HClO_4$ or buffer solution of $I = 0.5$ mol dm^{-3}, previously equilibrated to the desired temperature, and the cell quickly positioned in the thermostatted cell compartment of the spectrophotometer. The mixing time was often less than 10 s and the time lapse between mixing and the recording of the first measurement was often about 5 s. For the slower reactions the measurements were done in batches by the aliquot method. Pseudo-first-order rate constants were obtained from the raw kinetic data by the Guggenheim method[24] using a linear regression analysis computer program. Each rate constant reported is the arithmetic mean of at least two kinetic measurements. The faster reactions ($t_{\frac{1}{2}} < 15$ s) often required several repetitions in order to obtain reproducible $k_{obs.}$ values to within 5%. The ionic strength and solvent isotope effects were investigated under conditions identical to those described above.

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