#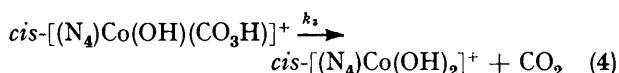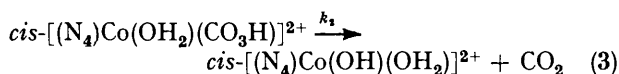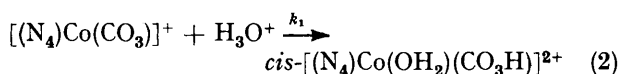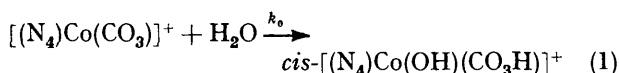 Kinetics and Mechanism of the Acid-catalysed Decarboxylation of the cis-Carbonato(5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Ion

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The acid-catalysed decarboxylation of the title compound has been studied over the range of perchloric acid concentrations 0.1—0.5 mol dm^{-3} at I = 0.5 mol dm^{-3} (Na[ClO$_4$]), and 25, 34.8, and 45.4 °C. Over this acidity range $k_{obs.}$ = k_0 + k_1[H$^+$]; however, the k_0 term does not make a significant contribution. The values of the activation parameters (for k_1) are $\Delta H^{\ddagger}$ = 82.9 kJ mol^{-1} and $\Delta S^{\ddagger}_{298}$ = −0.4 J K^{-1}mol^{-1}. The reaction exhibits a solvent deuterium-isotope effect k_{D_2O}/k_{H_2O} = 2.6 at 25 °C; the solvent deuterium-isotope effect is consistent with a rapid pre-equilibrium protonation followed by rate-determining ring opening, and excludes a mechanism involving concerted attack by [H$_3$O]$^+$. The value of $\Delta S^{\ddagger}$ close to zero, and the magnitude of the solvent isotope effect, suggests an A-1 type reaction to give a five-co-ordinate intermediate.

THE kinetics of the acid-catalysed aquation (or decarboxylation) of a number of carbonatotetraminecobalt(III) complexes have been investigated and discussed over recent years.[1-7] For such reactions the rate law normally observed is $k_{obs.}$ = k_0 + k_1[H$^+$], where $k_{obs.}$ is the observed first-order rate constant at constant hydrogen-ion concentration, and k_0 and k_1 are the rate constants for the parallel rate-determining carbonato ring-opening processes (1) and (2) below [(N$_4$) is a tetra-amine]. The decarboxylation steps

$$[(N_4)Co(CO_3)]^+ + H_2O \xrightarrow{k_0}$$
$$cis\text{-}[(N_4)Co(OH)(CO_3H)]^+ \quad (1)$$

$$[(N_4)Co(CO_3)]^+ + H_3O^+ \xrightarrow{k_1}$$
$$cis\text{-}[(N_4)Co(OH_2)(CO_3H)]^{2+} \quad (2)$$

$$cis\text{-}[(N_4)Co(OH_2)(CO_3H)]^{2+} \xrightarrow{k_2}$$
$$cis\text{-}[(N_4)Co(OH)(OH_2)]^{2+} + CO_2 \quad (3)$$

$$cis\text{-}[(N_4)Co(OH)(CO_3H)]^+ \xrightarrow{k_3}$$
$$cis\text{-}[(N_4)Co(OH)_2]^+ + CO_2 \quad (4)$$

represented by equations (3) and (4) are rapid, and the above reaction scheme is consistent with the observed kinetics if $k_2 \gg k_1$[H$_3$O$^+$] and $k_2 \gg k_3$.

The decarboxylation of a number of carbonato complexes of the type [CoL(CO$_3$)]$^{2+}$, where L represents the macrocyclic ligands C-rac-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (L^1 = tet-b),[1] 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L^2 = trans-Me$_6$[14]diene),[1] and 1,4,8,11-tetra-azacyclotetradecane (L^3 = cyclam)[5] have been studied.

The present paper is concerned with the acid-catalysed decarboxylation of [Co(L^4)(CO$_3$)]$^{2+}$. The work was undertaken to investigate the influence of steric effects and ligand unsaturation on decarboxylations of this type. Ligand unsaturation may lead to stabilisation of five-co-ordinate intermediates by d_π–p_π bonding. In addition, it was hoped that the determination of activation parameters and the solvent deuterium-isotope effect would clarify a number of problems connected with the intimate mechanism of the acid catalysis which require consideration.[6,8]

L^1

L^2

L^3

L^4
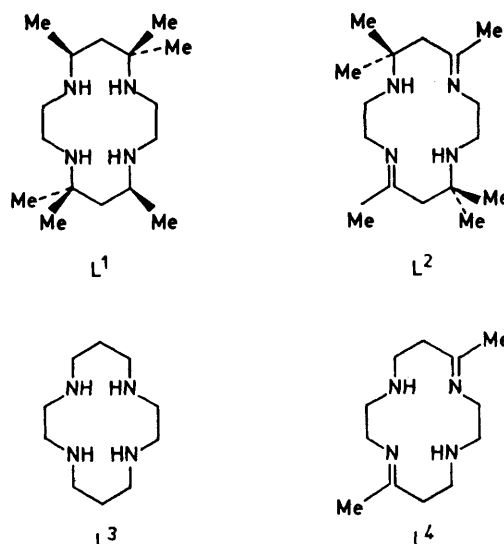
EXPERIMENTAL

cis-Carbonato(5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) perchlorate sesquihydrate, cis-[Co(L^4)(CO$_3$)][ClO$_4$]·1.5H$_2$O, was prepared as previously described [9] (Found: C, 33.15; H, 5.6; N, 11.9. Calc. for C$_{13}$H$_{27}$ClCoN$_4$O$_{8.5}$: C, 33.2; H, 5.8; N, 11.9%).

Synthesis.—The trans-diaqua(5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) cation was prepared by two routes; (a) by acid-catalysed ring opening of cis-[Co(L^4)(CO$_3$)]$^+$, and (b) by direct synthesis, and isolated as the perchlorate salt.

Method (a). cis-[Co(L^4)(CO$_3$)][ClO$_4$]·1.5H$_2$O (0.1 g) was dissolved in the minimum volume of perchloric acid (0.5 mol dm^{-3}) and the solution heated on a water-bath for ca. 5 min. The solution was then set aside at room temperature for ca. 1 week, during which time reddish green crystals began to appear. The product was filtered off, washed with cold ethanol and then ether, and dried in vacuo (Found: C, 22.6; H, 4.9; N, 8.4. C$_{12}$H$_{28}$Cl$_3$CoN$_4$O$_{14}$·1.5H$_2$O requires C, 22.35; H, 4.85; N, 8.7%).
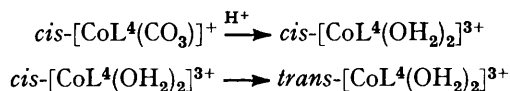
Method (b).—A solution of $L^4 \cdot 2HClO_4$ (4.25 g, 0.1 mol) in ethanol–water (50 cm³, 1 : 1 v/v) was added to a solution of $Co[ClO_4]_2 \cdot 6H_2O$ (3.66 g, 0.01 mol) in ethanol–water (50 cm³, 1 : 1 v/v) and the mixture heated on a steam-bath for *ca.* 1 h. During heating, air was passed through the mixture and this was continued for a further 3 h. The mixture was filtered and the filtrate made up to *ca.* 30% in $HClO_4$ and heated for a further 0.5 h. The volume of the solution was reduced on a rotary evaporator to *ca.* 30 cm³ and the solution set aside at room temperature. After several hours green crystals of the *product* appeared, which were filtered off, washed with cold ethanol and then ether, and dried *in vacuo* (Found: C, 21.9; H, 4.7; N, 8.6. $C_{12}H_{28}Cl_3CoN_4$-$O_{14} \cdot 2H_2O$ requires C, 22.05; H, 4.9; N, 8.6%).

Kinetics.—The reactions were monitored spectrophotometrically by following the decrease in absorbance at 280 nm. Linear plots of log $(A_t - A_\infty)$ *vs.* time t were observed in all cases. The reactions were carried out at $I = 0.5$ mol dm⁻³, the ionic strength being adjusted by the addition of sodium perchlorate. The concentration of the perchloric acid solutions was determined by titration with standard sodium hydroxide solution. Kinetic measurements were carried out with a Gilford 2400S instrument, the cell temperature being maintained to within 0.05 °C by circulating water through a metal cell-block holder. The temperature was monitored throughout the reaction, and each kinetic measurement was carried out in triplicate. Routine u.v.–visible spectral measurements, including interval scan spectra, were made with a Perkin-Elmer 402 instrument.

RESULTS AND DISCUSSION

The complex *cis*-$[CoL^4(CO_3)]^+$ has $\lambda_{max.}$ 504 ($\varepsilon = 133$ dm³ mol⁻¹ cm⁻¹) and 360 nm (167 dm³ mol⁻¹ cm⁻¹). In acidic solution (0.1—0.5 mol dm⁻³ $H[ClO_4]$) the absorbance decreases with time at both wavelengths with the band at 504 nm moving to *ca.* 490 nm. The resulting spectrum is consistent with the formation of a *cis*-diaqua-complex. Thus *cis*-$[CoL^3(OH_2)_2]^{3+}$ has $\lambda_{max.}$ 506 ($\varepsilon = 110$) and 367 nm (99).[10] This relatively rapid reaction is followed by a much slower reaction, in which the absorbance decreases with time, suggesting isomerisation to the *trans*-diaqua-complex. The final product has $\lambda_{max.}$ 362 ($\varepsilon = 79$), 424 (49), and 564 nm (27). This spectrum is identical to that of an authentic sample of *trans*-$[CoL^4(OH_2)_2]^{3+}$, which has $\lambda_{max.}$ 362 ($\varepsilon = 77$), 424 (48), and 564 nm (26).

The spectral changes are thus consistent with the reaction scheme;

$$cis\text{-}[CoL^4(CO_3)]^+ \xrightarrow{H^+} cis\text{-}[CoL^4(OH_2)_2]^{3+}$$

$$cis\text{-}[CoL^4(OH_2)_2]^{3+} \longrightarrow trans\text{-}[CoL^4(OH_2)_2]^{3+}$$

The kinetics of the acid-catalysed ring-opening step were monitored spectrophotometrically using the decrease in absorbance at 280 nm. As the isomerisation reaction is very slow, it was possible to obtain values of A_∞ with little difficulty. The acid-catalysed aquation was studied over the range of perchloric acid concentrations 0.1—0.5 mol dm⁻³, at $I = 0.5$ mol dm⁻³, adjusted with sodium perchlorate. Values of $k_{obs.}$ (the observed first-order rate constant at constant hydrogen-ion concen-

tration) were obtained from plots of log $(A_t - A_\infty)$ which were linear in every case. The rate constants $k_{obs.}$ at 25, 34.8, and 45.4 °C are listed in Table 1.

TABLE 1

Kinetic data for the acid-catalysed aquation of *cis*-$[CoL^4(CO_3)]^+$ at $I = 0.5$ mol dm⁻³ ($Na[ClO_4]$) †

25 °C

[HClO₄]/ mol dm⁻³	$10^3 k_{obs.}/s^{-1}$
0.099	1.67
0.196	2.90
0.320	4.78
0.400	5.93
0.500	7.33

$k_1 = 1.46 \times 10^{-2}$ dm³ mol⁻¹ s⁻¹; $k_0 = 7.5 \times 10^{-5}$ s⁻¹

34.8 °C

[HClO₄]/ mol dm⁻³	$10^3 k_{obs.}/s^{-1}$
0.050	2.55
0.099	4.73
0.151	7.49
0.196	9.38
0.250	10.98
0.320	12.76
0.400	18.65

$k_1 = 4.25 \times 10^{-2}$ dm³ mol⁻¹ s⁻¹; $k_0 = 6.34 \times 10^{-4}$ s⁻¹

45.4 °C

[HClO₄]/ mol dm⁻³	$10^3 k_{obs.}/s^{-1}$
0.050	7.07
0.099	15.36
0.151	20.33
0.196	25.40
0.250	35.04
0.320	42.84

$k_1 = 12.89 \times 10^{-2}$ dm³ mol⁻¹ s⁻¹; $k_0 = 1.59 \times 10^{-3}$ s⁻¹

† Values of k_1 and k_0 were obtained by linear regression analysis; the k_0 constants are subject to considerable error, and must be regarded as order-of-magnitude values only.

Values of $k_{obs.}$ are almost directly proportional to [H⁺] over the acidity range studied, indicating that k_0 does not make a significant contribution to the overall reaction. Linear regression analysis gives $k_1 = 1.46 \times 10^{-2}$ dm³ mol⁻¹ s⁻¹ and $k_0 = 7.5 \times 10^{-5}$ s⁻¹ at 25 °C. At the acidities used in the present study it is difficult to determine k_0 with any degree of precision. Attempts to determine k_0 at lower acidities were frustrated by the *cis→trans* isomerisation reaction of the diaqua-species. Dasgupta [5] has reported a small contribution from k_0 in the ring-opening of $[CoL^3(CO_3)]^+$ where $k_0 = 2.5 \times 10^{-4}$ s⁻¹ and $k_1 = 7.1 \times 10^{-3}$ dm³ mol⁻¹ s⁻¹ at 40 °C. The requisite constants k_1 at 34.8 and 45.4 °C are 4.25×10^{-2} dm³ mol⁻¹ s⁻¹ and 12.89×10^{-2} dm³ mol⁻¹ s⁻¹. The appropriate activation parameters are $\Delta H^{\ddagger} = 82.9$ kJ mol⁻¹ and $\Delta S^{\ddagger}_{298} = -0.4$ J K⁻¹ mol⁻¹. At 25 °C, the rate of the acid-catalysed aquation of the L^4 complex is *ca.* twice that for L^2 and *ca.* 11.5 times faster than for L^3 (see Table 2). The activation parameters for the acid-catalysed decarboxylations of the macrocyclic complexes (Table 2) are quite similar with $\Delta H^{\ddagger}$ *ca.* 85 kJ mol⁻¹ and $\Delta S^{\ddagger}_{298}$ close to zero. Steric effects appear to be unimportant; however, complexes containing unsaturated ligands do decarboxylate rather faster than the cyclam derivative.

Mechanism (A)
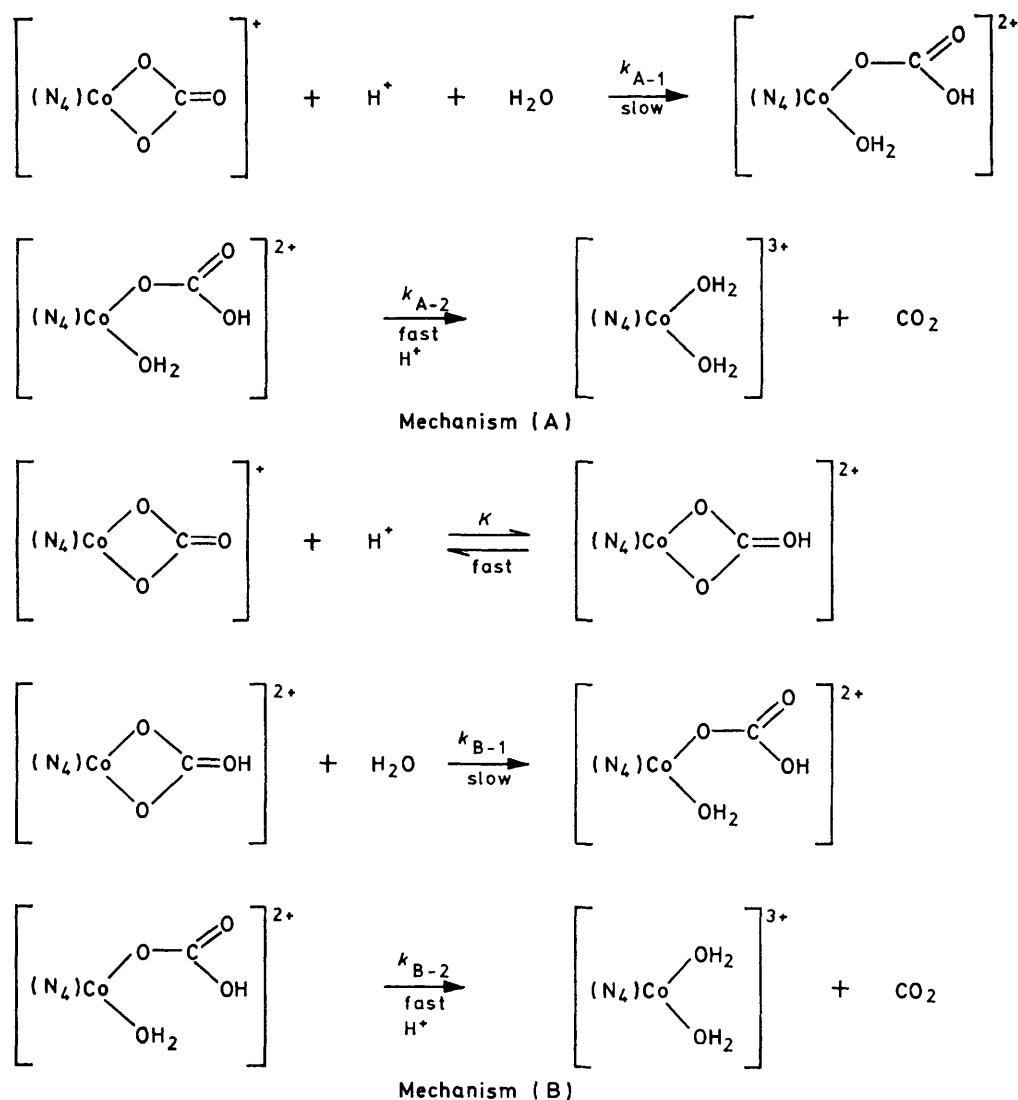
Mechanism (B)

(N$_4$) denotes the macrocyclic ligand

SCHEME Possible mechanisms for acid-catalysed decarboxylation

The intimate mechanism of the acid catalysis requires consideration. Early work by Sastri and Harris [7] favoured a mechanism in which there is rate-determining proton transfer from hydronium ion to the carbonato-moiety in the transition state, leading to ring-opening by metal-oxygen bond cleavage [Mechanism (A), Scheme]. An alternative mechanism involves rapid pre-equilibrium protonation of the complex followed by rate-determining ring opening [Mechanism (B), Scheme]. It is possible to distinguish between these two mechanisms by using solvent deuterium-isotope effects. For mechanism (A) a rate-determining proton-transfer step is involved and $k_{D_2O}/k_{H_2O} < 1$. In mechanism (B), $k_{D_2O}/k_{H_2O} > 1$ since D_2O is less basic than water, and hence the substrate will be able to compete with the solvent for the deuteron in D_2O more effectively than for the proton in H_2O.

For solutions ca. 0.5 mol dm^{-3} in hydrogen ion at 25 °C,

the value of $k_{D_2O}/k_{H_2O} = 2.6$ (Table 3), fully consistent with a rapid pre-equilibrium protonation. More recent work by Harris and his co-workers [6] has established that k_{D_2O}/k_{H_2O} for the acid-catalysed decarboxylation of the carbonatotetrakis(pyridine)cobalt(III) ion falls in the range 1.7—1.9, while a re-investigation [8] of the solvent deuterium-isotope effect for the acid-catalysed decarb-

TABLE 2

Rate constants and activation parameters for the acid-catalysed decarboxylation of macrocyclic [CoL(CO$_3$)]$^+$ complexes [a]

Ligand	$k_1/$ dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger}/$ kJ mol^{-1}	$\Delta S^{\ddagger}/$ J K^{-1} mol^{-1}	Ref.
Me$_2$[14]diene (L^4)	1.5 × 10^{-2}	82.9	−0.4	This work
Me$_6$[14]diene (L^2)	8.0 × 10^{-3}	88.6 [b]	+3.8 [b]	1
Cyclam (L^3)	1.3 × 10^{-3}	86.2	−10.9	5

[a] Values of k_1 at 25 °C. [b] Calculated from Kernohan and Endicott (ref. 1).

TABLE 3

Solvent deuterium-isotope effect at 25 °C [a]

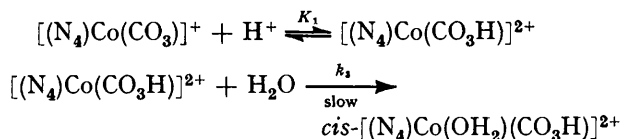| [HCl]/mol dm^{-3}	$10^3 k_{obs.}/s^{-1}$	$10^2 k_{obs.}[H^+]^{-1}/$ dm^3 mol^{-1} s^{-1}
0.493	8.3 [b]	1.68
[DCl]/mol dm^{-3}	23.7 [b]	4.35

$$k_{H_2O}/k_{D_2O} = 2.6$$

[a] The small contribution of k_0 to $k_{obs.}$ was ignored in the calculation of the isotope effect. [b] Mean of three kinetic runs.

oxylation of [Co(en)$_2$(CO$_3$)]$^+$ gave a value of 2.3. There is now considerable evidence to support the view that acid-catalysed decarboxylations of carbonato-complexes occur by a rapid pre-equilibrium protonation, followed by a slow rate-determining ring-opening.

The reaction could occur by either an A-1 or an A-2 type mechanism. For an A-1 reaction;

$$[(N_4)Co(CO_3)]^+ + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} [(N_4)Co(CO_3H)]^{2+}$$

$$[(N_4)Co(CO_3H)]^{2+} \xrightarrow[slow]{k_2} [(N_4)Co(OCO_2H)]^{2+}$$
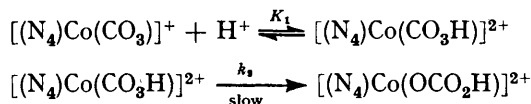
and the rate constant $k_1 = K_1 k_2$; while for the A-2 situation,

$$[(N_4)Co(CO_3)]^+ + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} [(N_4)Co(CO_3H)]^{2+}$$

$$[(N_4)Co(CO_3H)]^{2+} + H_2O \xrightarrow[slow]{k_3}$$

$$cis\text{-}[(N_4)Co(OH_2)(CO_3H)]^{2+}$$

and $k_1 = K_1 k_3[OH_2]$. The A-1 mechanism would involve decomposition of the protonated species to give a five-co-ordinate intermediate, while the A-2 mechanism

would involve nucleophilic attack by water on the protonated species. For the A-1 reaction the entropy of activation is close to zero since the reaction is unimolecular, while A-2 reactions have substantial negative entropies of activation since they are bimolecular. For A-1 reactions the rate of the reaction at very low acidities is proportional to the hydrogen-ion concentration and at higher acidities to h_0 (*i.e.* a plot of log $k_{obs.}$ *vs.* $- H_0$ is linear with a slope of unity, where $H_0 = -\log h_0$). The acid-catalysed hydrolysis of *cis*-[CoL^4(CO$_3$)]$^+$ displays a solvent deuterium-isotope effect k_{D_2O}/k_{H_2O} of 2.6. This ratio is in the range (1.9—2.6) considered typical [10] for A-1 type hydrolysis, and is much larger than the values of 1.3—1.4 which have been observed [10] for A-2 reactions. The present evidence thus favours an A-1 mechanism.

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