Kinetics and Mechanism of the Base Hydrolysis of the *cis*-Chlorobis(ethylenediamine)(imidazole)cobalt(III) Cation

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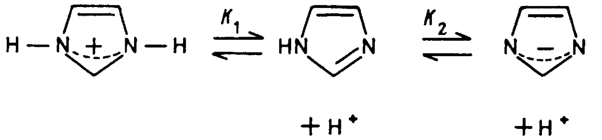
Base hydrolysis of *cis*-$[CoCl(en)_2(imH)]^{2+}$ (en = ethylenediamine, imH = imidazole) has been studied over the range pH 8.26—9.74 at I = 0.1 mol dm^{-3} (Na[ClO$_4$]) and 25 °C. In this pH range the reaction is first order in the hydroxide-ion concentration (k_{OH} 29 ± 3 dm^3 mol^{-1} s^{-1}). At higher pH (9.89—12.89) the reaction displays less than a first-order dependence on the [OH$^-$] due to conversion into the conjugate base *cis*-$[CoCl(en)_2(im)]^+$ (im$^-$ = deprotonated imidazole). The pK_a for this ionisation is 10.5 at I = 0.1 mol dm^{-3}. At still higher pH the values of $k_{obs.}$ do not become constant, but increase as the pH is increased, consistent with the formation of a second conjugate base by deprotonation of an ethylenediamine ligand. The activation parameters for base hydrolysis at low pH are $\Delta H^\ddagger$ = 91.2 kJ mol^{-1} and $\Delta S^\ddagger$ (298 K) = 89 J K^{-1} mol^{-1}. The substantial positive $\Delta S^\ddagger$ is fully consistent with an S_N1(CB) mechanism.

THE complex *cis*-$[CoCl(en)_2(imH)]^{2+}$ (en = ethylenediamine; imH = imidazole, im$^-$ = deprotonated imidazole) was first reported by Kindred and House [1] who also resolved the complex. Aquation rates in 1.0 mol dm^{-3} HNO$_3$ over a temperature range have been reported [2] and further kinetic investigations of acid and base hydrolysis have been carried out by Dash and Mohapatra.[3]

Imidazole is a weak acid and the proton ionisation equilibria may be represented as below. The reported values of pK_1 and pK_2 are 7.2 (26 °C) [4] and 14.6 (25 °C) [5]



respectively. Imidazole normally co-ordinates to metal ions *via* the pyridine nitrogen,[6] although it has recently been suggested [7] that imidazole is an ambidentate ligand which can also bind *via* the pyrrole nitrogen. It is of interest to establish to what extent this biologically important ligand and its imido-base labilises the co-ordination sphere of metal ions in their complexes. It would be expected that co-ordination of imidazole to a metal ion would lead to a significant decrease in the value of pK_2, thus $[Co(imH)_4]^{2+}$ has a pK_a of 12.5,[6] and $[Co(hist)_2]^{2+}$ (hist = histamine) a pK_a of 13.[6] When the present work was in progress a pK_a of 9.25 ± 0.05 was reported [3] for *cis*-$[CoCl(en)_2(imH)]^{2+}$ at 31.8 °C and I = 0.3 mol dm^{-3}. This value seems quite low, and is comparable with that of $[Ru(NH_3)_5(imH)]^{3+}$ for which pK_a = 8.9 ± 0.1.[8] Harrowfield *et al.*[9] have recently determined a pK_a of 10.02 for $[Co(NH_3)_5(imH)]^{3+}$ at I = 1.0 mol dm^{-3} and 25 °C, and as a result it seems probable that for *cis*-$[CoCl(en)_2(imH)]^{2+}$ the pK_a will lie in the range 10—12. Complete formation of the conjugate base should therefore occur at pH <14. Deprotonated imidazole should be capable of labilising the Co–Cl bond and stabilising the five-co-ordinate intermediate in an S_N1(CB) process, and it is of interest to determine its effectiveness in this type of reaction.

Although a number of reports [10,11] have appeared suggesting essentially complete conversion into the conjugate base in complexes of the type *cis*-$[CoCl(en)_2(amine)]^{2+}$ (amine = aniline, *m*- or *p*-toluidine, or 3,4-dimethylaniline), generally, pK_a data are lacking and investigations have not been extended to the high pH range.

EXPERIMENTAL

The complex *cis*-chlorobis(ethylenediamine)(imidazole)cobalt(III) chloride was prepared as previously described.[1] The crude product was recrystallised from very dilute hydrochloric acid at 60 °C. Crystallisation was initiated by the addition of a few drops of HCl (12 mol dm^{-3}) followed by cooling in ice. The crystals were washed with ethanol then diethyl ether and dried *in vacuo* (Found: C, 23.6; H, 5.7; N, 23.9. Calc. for $C_7H_{20}Cl_3CoN_6$: C, 23.7; H, 5.7; N, 23.8%).

Solutions of the *cis*-aquabis(ethylenediamine)(imidazole)cobalt(III) ion were prepared either by mercury(II)-promoted aquation in dilute HClO$_4$ or HNO$_3$ essentially as previously described,[12] or by stirring a solution of the chloro-complex with 3 mol equivalents of silver(I) perchlorate in aqueous solution and filtering off the precipitated silver chloride. The solutions so obtained were diluted to the requisite concentrations, and where necessary adjusted to the appropriate ionic strength with sodium perchlorate.

Ionisation of Imidazole.—The chloro-complex (180 mg, 5.09 × 10^{-4} mol) was dissolved in potassium chloride solution (70 cm^3 of 0.1 mol dm^{-3}) and several drops of concentrated sodium hydroxide solution added to bring the pH to 9.0 on a Radiometer TTT2 pH-stat. The solution was allowed to hydrolyse at pH 9.0 for 1 h at 25 °C. On completion of the hydrolysis, portions of solid powdered Na[OH] were added to increase the pH. The solution was purged with nitrogen throughout the measurement. Aliquots were removed and the absorbance immediately determined at 345 and 500 nm using a Gilford 2400S instrument. Scan spectra were also recorded on a Perkin-Elmer 402 spectrophotometer over the range 310—670 nm.

Kinetics.—The kinetics of base hydrolysis in the range pH 8.26—9.74 at 25 °C were monitored spectrophotometrically at 315 nm using a Gilford 2400S instrument. The pH was controlled with NH(CH$_2$CH$_2$OH)$_2$–HCl buffers,[13] adjusted to I = 0.1 mol dm^{-3} with Na[ClO$_4$]. Measurements in the range pH 9.89—11.13 were made using n-butylamine–HCl buffers.[13] Each kinetic determination was carried out in triplicate. The observed rate constants

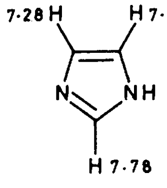
($k_{obs.}$) at constant pH were obtained from plots of log ($A_\infty - A_t$) against time. Values of the hydroxide-ion concentration were determined from the pH using a molar activity coefficient of 0.774 and a value of $pK_w = 14.00$ at 25 °C.[14]

Since there was a tendency for A_∞ values to drift at higher temperatures (presumably due to a slow *cis* $\rightleftharpoons$ *trans* isomerisation), the kinetics at the additional temperatures of 30, 35, and 45 °C were monitored by pH-stat (Radiometer TTT2). A type G202B high-alkalinity glass electrode was used as indicator electrode and a type K401 saturated calomel electrode (s.c.e.) with diffusion filter as reference electrode. The electrode system was standardised at the appropriate temperature using the recommended NBS buffer standards.[14] The ionic strength (0.1 mol dm^{-3}) was maintained with potassium chloride solution. The general technique employed in the pH-stat measurements has been outlined.[15] Excellent agreement was obtained between the spectrophotometric and pH-stat rate constants. Thus at 25 °C, $k_{obs.} = 1.14 \times 10^{-3}$ s^{-1} and $k_{OH} = 28$ dm^3 mol^{-1} s^{-1} by pH stat, while $k_{obs.} = 1.17 \times 10^{-3}$ s^{-1} and $k_{OH} = 28.2$ dm^3 mol^{-1} s^{-1} spectrophotometrically. In the pH-stat measurements, values of the hydroxide-ion concentration were estimated using activity coefficients determined from the Davies' equation [16] [0.770 (30), 0.768 (35), and 0.764 (45 °C)] and appropriate values of pK_w [13.883 (30), 13.680 (35), and 13.396 (45 °C)].

The stopped-flow measurements were carried out using Durrum-Gibson and Canterbury SF-3A instruments with sodium hydroxide solutions and KCl as the supporting electrolyte.

RESULTS AND DISCUSSION

The complex *cis*-[CoCl(en)$_2$(imidazole)]$^{2+}$ was prepared essentially by the procedure first described by Bailar and Clapp.[17] A variety of physical measurements including optical resolution support the assignment of the *cis* configuration. The complex has $\lambda_{max.}$ 524 (ε 79) and 362 nm (ε 99 dm^3 mol^{-1} cm^{-1}) in good agreement with the literature values;[1,3] and the band intensities are fully consistent with a *cis*-configuration.[18] The ^{1}H n.m.r. spectrum in D$_2$O solution has a signal at δ 2.9—2.95 p.p.m. assigned to the methylene protons of the ethylenediamine rings. For the *trans* isomer this signal occurs at >3 p.p.m.[19] The imidazole protons occur at 7.26, 7.40, and 8.24 p.p.m. For free imidazole the proton signals are assigned as shown in (I).[20] Electron withdrawal by Co^{III} leads to marked deshielding of the protons adjacent to the pyridine nitrogen.



(I)

The complex [Co(en)$_2$(imH)(OH$_2$)]$^{3+}$, prepared by mercury(II)-promoted aquation in 0.1 mol dm^{-3} nitric acid, which normally occurs with retention of configuration, has $\lambda_{max.}$ 484 (ε 95) and 345 (sh) nm (ε 120 dm^3 mol^{-1} cm^{-1}) in reasonable agreement with the literature values.[1] The lowest-energy band moves to 500 nm (ε 93 dm^3 mol^{-1} cm^{-1}) on formation of the penta-aminehydroxo-species. Further addition of base leads to a significant increase in the absorbance at 360 nm which can be attributed to formation of the conjugate base by deprotonation of imidazole.

Potentiometric titration of *cis*-[Co(en)$_2$(imH)(OH$_2$)]$^{3+}$ (*ca.* 5×10^{-3} mol dm^{-3} in 0.1 mol dm^{-3} K[NO$_3$]) with potassium hydroxide was carried out. A single inflection was observed in the titration curve after addition of one equivalent of base. This ionisation process can be attributed to equilibrium (1).

$$cis\text{-}[\mathrm{Co(en)_2(imH)(OH_2)}]^{3+} \rightleftharpoons cis\text{-}[\mathrm{Co(en)_2(imH)(OH)}]^{2+} + \mathrm{H}^+ \quad (1)$$

The pH-titration data were analysed essentially as described by Albert and Serjeant [21] to give $pK_a^p = 6.28 \pm 0.03$ at 25 °C and $I = 0.1$ mol dm^{-3}. (pK_a^p is a practical ionisation constant defined in terms of the activity of the hydrogen ion and the concentrations of the other species, *i.e.* $pK_a^p = a_{H^+}[A^-]/[HA]$.) The pK_a value is fully consistent with ionisation of the co-ordinated water molecule; thus for the ionisation of *cis*-[Co(en)$_2$(NMeH$_2$)(OH$_2$)]$^{3+}$ the reported [18] value of pK_a is 6.5 at 25 °C and $I = 0.1$ mol dm^{-3}. No evidence was obtained from the potentiometric data for a second ionisation process with a pK_a in the range 8—9 as would be expected from the data of Dash and Mohapatra.[3]

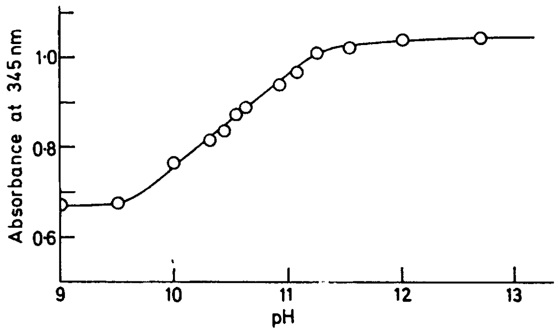


FIGURE 1 Spectrophotometric titration of *cis*-[Co(en)$_2$(imH)(OH)]$^{2+}$ at 345 nm

Spectrophotometric measurements established that a significant increase in the absorbance of the penta-aminehydroxo-complex occurred at 360 nm as the pH was increased from 9.0 to 12.0, and that this increase was paralleled by a much smaller absorbance increase at 500 nm. The spectral changes are reminiscent of those reported [11] for the anilinebis(ethylenediamine)hydroxocobalt(III) ion on conversion into the conjugate base. A spectrophotometric titration at $I = 0.1$ mol dm^{-3} and 25 °C over the range pH 9—12.0 (Figure 1) is consistent with a pK_a^p of 10.52 ± 0.05 (Table 1). This value may be compared with the pK_a of 10.02 for [Co(NH$_3$)$_5$(imH)]$^{3+}$ at $I = 1.0$ mol dm^{-3} and 25 °C.[9] The pK_a for *cis*-[CoCl(en)$_2$(imH)]$^{2+}$ would not be expected to be markedly different from that of *cis*-$[Co(en)_2(imH)(OH)]^{2+}$ since both complexes are of a similar charge type.

Kinetics.—The kinetics of base hydrolysis of *cis*-$[CoCl(en)_2(imH)]^{2+}$ were studied at 25 °C in the range pH 8.26—9.74 using $NH(CH_2CH_2OH)_2$–HCl buffers adjusted to $I = 0.1$ mol dm^{-3} (Table 2). The reactions were monitored spectrophotometrically at 315 nm. Values of $k_{OH} = k_{obs.}/[OH^-]$ are constant throughout this pH range ($k_{obs.}$ is the observed first-order rate constant at constant pH) giving a value of $k_{OH} = 29 \pm 3$ dm^3 mol^{-1} s^{-1} at 25 °C and $I = 0.1$ mol dm^{-3}. The clean first-order dependence on the hydroxide-ion concentration over this pH range confirms that significant (*i.e.* >10%) concentrations of the conjugate base are absent.

TABLE 1

pK_a of *cis*-$[Co(en)_2(imH)(OH)]^{2+}$ at 25 °C and $I = 0.1$ mol dm^{-3} (KCl) [a]

pH	A_{345} [b]	A_{500} [b]	%A [c]	%HA [c]	pK_a [c]
9.00	0.672 (92.4)	0.677 (93)			
9.50	0.677	0.682			
10.03	0.770	0.688	26.5	73.5	10.47
10.34	0.812	0.689	37.8	62.2	10.55
10.45	0.833	0.704	43.5	56.5	10.56
10.56	0.872	0.710	54.1	45.9	10.49
10.69	0.888	0.723	58.4	41.6	10.54
10.96	0.946	0.712	74.1	25.9	10.50
11.10	0.968	0.716	80.0	20.0	10.50
11.25	1.015	0.720			pK_a = 10.52 ± 0.05
11.55	1.020	0.710			
11.83	1.033	0.718			
12.05	1.041	0.715			
12.70	1.042 (143.3)	0.715 (98.3)			

[a] Complex concentration, 7.27×10^{-3} mol dm^{-3}. [b] Absorbance for a 1-cm cell; values in parentheses are absorption coefficients (dm^3 mol^{-1} cm^{-1}). [c] Calculated from the absorbances at 345 nm; A is the deprotonated complex *cis*-$[Co(en)_2(im)(OH)]^+$ and HA the complex *cis*-$[Co(en)_2(imH)(OH)]^{2+}$.

TABLE 2

Kinetics of base hydrolysis of *cis*-$[CoCl(en)_2(imH)]^{2+}$ in buffer solutions at 25 °C and $I = 0.1$ mol dm^{-3} ($Na[ClO_4]$) monitored at 315 nm

(*a*) Low pH [a]

pH	$10^4\ k_{obs.}$/s^{-1}	k_{OH}/dm^3 mol^{-1} s^{-1}
8.26	0.77	32.5
8.46	1.08	28.8
8.51	1.11	26.3
8.75	2.18	29.8
8.82	2.70	31.3
8.96	3.60	30.5
9.38	10.93	34.3
9.50	11.66	28.2
9.74	20.93	29.2

$k_{OH} = 29 \pm 3$ dm^3 mol^{-1} s^{-1}

(*b*) High pH

pH	$[OH^-]$/mol dm^{-3}	$k_{obs.}$/s^{-1}	k_{OH}/dm^3 mol^{-1} s^{-1}
9.89 [a]	1.01×10^{-4}	2.80×10^{-3}	27.6
10.18 [b]	1.97×10^{-4}	4.55×10^{-3}	23.1
10.77 [b]	7.68×10^{-4}	7.35×10^{-3}	9.6
11.13 [b]	1.76×10^{-3}	1.19×10^{-2}	6.8
11.89 [c]	1.00×10^{-2}	3.05×10^{-2}	3.1
12.58 [c,d]	5.00×10^{-2}	2.15×10^{-1}	4.3
12.89 [c,d]	1.00×10^{-1}	3.22×10^{-1}	3.2

[a] $NH(CH_2CH_2OH)_2$–HCl buffers. [b] n-Butylamine–HCl buffers. [c] Sodium hydroxide solutions. [d] Stopped-flow measurement.

TABLE 3

Temperature dependence of the base hydrolysis in the range pH 8.7—9.5 at $I = 0.1$ mol dm^{-3} (KCl) *

θ_c/°C	pH	$10^5\ [OH^-]$/ mol dm^{-3}	$10^3\ k_{obs.}$/s^{-1}	k_{OH}/ dm^3 mol^{-1} s^{-1}
25	9.50	4.12	1.14	28
30	9.10	2.14	1.27	59
	9.18	2.57	1.40	55
35	9.18	4.11	4.22	102
	9.17	4.02	4.12	102
45	8.70	2.63	8.59	326
	8.78	3.17	10.14	320

θ_c/°C	k_{OH}/dm^3 mol^{-1} s^{-1}
25	29
30	57
35	102
45	323

$\Delta H^\ddagger = 91.2$ kJ mol^{-1}
$\Delta S^\ddagger$ (298 K) $= 89$ J K^{-1} mol^{-1}

* Reactions monitored by pH-stat.

The temperature dependence of the reaction in the range pH 8.7—9.5 was studied by pH-stat at the additional temperatures of 30, 35, and 45 °C (Table 3).

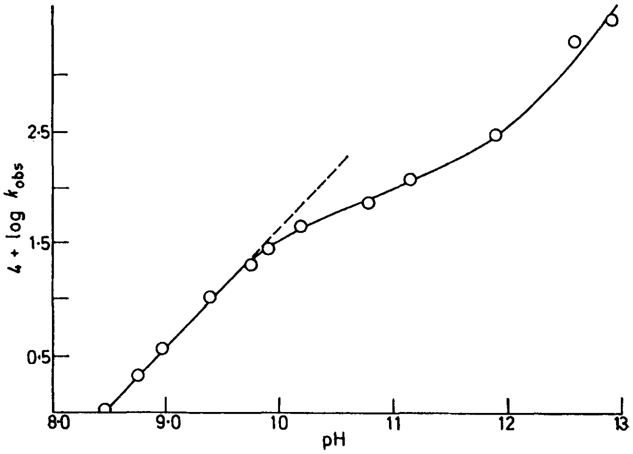


FIGURE 2 pH–Rate profile for the hydrolysis of *cis*-$[CoCl(en)_2(imH)]^{2+}$. The broken line is that of unit gradient

Values of k_{OH} were determined by pH-stat, since at higher temperatures there was a tendency for the infinity absorbance to drift, presumably as a result of a slow *cis* $\rightleftharpoons$ *trans* isomerisation. The appropriate activation parameters are $\Delta H^\ddagger = 91.2$ kJ mol^{-1} and $\Delta S^\ddagger$ (298 K) $= 89$ J K^{-1} mol^{-1}. Edwards *et al.*[22] have reviewed the activation parameters for octahedral substitutions and have concluded that for an S_N2 reaction $\Delta S^\ddagger \sim -62$ J K^{-1} mol^{-1} while for an S_N1(CB) mechanism $\Delta S^\ddagger \sim 142$ J K^{-1} mol^{-1}. The present results are consistent with an S_N1(CB) mechanism, where the experimental values normally fall within the range 84—167 J K^{-1} mol^{-1}.

Base hydrolysis of the imidazole complex is *ca.* 2.5 times faster than for the *cis*-$[CoCl(en)_2(NRH_2)]^{2+}$ complexes at 25 °C where $k_{OH} = 12.7$ dm^3 mol^{-1} s^{-1} at 25 °C and $I = 0.1$ mol dm^{-3} (R = Me, Et, Pr^n, or Bu^n).[18]

Further studies of the base-hydrolysis reaction were carried out in the range pH 9.89—12.89 using either n-butylamine–HCl buffers or sodium hydroxide solutions. Values of $k_{\text{obs.}}$ are listed in Table 1. In this pH range the reaction does not show a first-order dependence on the hydroxide-ion concentration. A plot of log $k_{\text{obs.}}$ against pH shows a divergence from unit gradient at pH >*ca.* 9.7. At such pH values ionisation of the imidazole proton to form the conjugate base ($\text{p}K_a$ 10.5) becomes significant. However, the values of $k_{\text{obs.}}$ do not become constant, but increase as the pH is increased. This type of behaviour could be due to the formation of two conjugate bases in solution which could be represented by the equilibria (2) and (3).

$$cis\text{-}[\text{CoCl(en)}_2(\text{imH})]^{2+} \rightleftharpoons cis\text{-}[\text{CoCl(en)}_2(\text{im})]^{+} + \text{H}^{+} \quad (2)$$

$$cis\text{-}[\text{CoCl(en)}_2(\text{im})]^{+} \rightleftharpoons cis\text{-}[\text{CoCl(en)(en} - \text{H)(im)}] + \text{H}^{+} \quad (3)$$

Fenemor and House [23] have studied the steric course of the base hydrolysis of some Λ-*cis*-$[\text{CoCl(en)}_2(\text{amine})]^{2+}$ complexes in 0.025 mol dm^{-3} Na[OH] (pH *ca.* 12.4). If deprotonation occurred exclusively at the imidazole ligand, the products would be 33% *trans*- and 66% Λ-*cis*-penta-aminehydroxo-complex. The observed values are 21% *trans*, 23% Λ-*cis*, and 56% racemisation (ΔΛ). A scheme involving 50% *trans*-amine and 50% *trans*-Cl deprotonation would give *ca.* 16% *trans*, 58% Λ-*cis*, and 25% Δ-*cis*, corresponding to 16% isomerisation, 50% racemisation, and 33% optical retention. A high degree of optical retention was observed with the benzimidazole complex suggesting that deprotonation at the NH proton on the benzimidazole ligand could be of importance, and this view is supported by recent kinetic studies.[24,25] The present kinetic results suggest that the stereochemical course of the reaction will be pH-dependent. At low pH, deprotonation at imidazole will give a conjugate base which should provide a significant route to the penta-aminehydroxo-complex, while at higher pH the product will also be derived from the conjugate base obtained by deprotonation of an ethylenediamine ligand.

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