Kinetics and Mechanism of Hydrolysis of *cis*-Chlorobis(ethylenediamine)(imidazole)cobalt(III) and *cis*-Bromobis(ethylenediamine)(imidazole)cobalt(III) Cations

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The kinetics of hydrolysis of *cis*-$[CoX(imH)(en)_2]^{2+}$ (imH = imidazole; en = ethylenediamine; X = Cl or Br) cations have been investigated in perchlorate medium of $I = 0.3$ mol dm^{-3}. In the range pH 0.5—5.7 the rate law for aquation takes the form $-d\ln[Co^{III}]/dt = k_1 + k_2K_{NH}[H^+]^{-1}$ where k_1 and k_2 are the aquation rate constants of $[CoX(en)_2(imH)]^{2+}$ and $[CoX(im)(en)_2]^+$ respectively and K_{NH} is the acid dissociation constant of the co-ordinated imidazole. At 50 °C the values of k_1, k_2K_{NH}, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ for the k_1 path are $(1.21 \pm 0.02) \times 10^{-5}$ s^{-1}, $(4.95 \pm 0.11) \times 10^{-11}$ mol dm^{-3} s^{-1}, 92.3 ± 1.2 kJ mol^{-1}, −54 ± 3 J K^{-1} mol^{-1} for the chloro-, and $(5.52 \pm 0.10) \times 10^{-5}$ s^{-1}, $(33.4 \pm 0.7) \times 10^{-11}$ mol dm^{-3} s^{-1}, 94.5 ± 0.3 kJ mol^{-1}, and −34 ± 1 J K^{-1} mol^{-1} for the bromo-complex respectively. Values of k_2 obtained from the base-hydrolysis studies are $(1.28 \pm 0.17) \times 10^{-2}$ and $(2.46 \pm 0.22) \times 10^{-2}$ s^{-1} at 31.8 °C for the chloro- and bromo-complexes respectively, and the imido-complex $[CoCl(im)(en)_2]^+$ also undergoes second-order base hydrolysis with a rate constant of 5.1 ± 1.0 dm^3 mol^{-1} s^{-1} at the same temperature. The labilizing action of imidazole and its conjugate base on the Co–X bond appears to be comparable to that of pyridine and hydroxide respectively. Co-ordinated imidazole is 10^5 times stronger as an acid than free imidazole. The sulphate- and mercury(II)-catalysed aquations of both the substrates have also been studied. The value of k_{ip}/k_1, where k_{ip} and k_1 are the rate constants of aquation of $[CoX(imH)(en)_2]^{2+}$, $[SO_4]^{2-}$ and $[CoX(imH)(en)_2]^{2+}$ species respectively, is 2.3 ± 0.2 at 60 °C for X = Cl and 4.6 ± 0.1 at 50 °C for X = Br. The mercury(II)-catalysed aquation follows second-order kinetics, $-d\ln[Co^{III}]/dt = k_{Hg}[Hg^{2+}]$: at 30.5 °C the rate constant (k_{Hg}) and activation enthalpy and entropy are $(3.48 \pm 0.03) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, 68.4 ± 0.7 kJ mol^{-1}, and −48 ± 2 J K^{-1} mol^{-1} for the chloro- and 12.4 ± 0.5 dm^3 mol^{-1} s^{-1}, 53.4 ± 0.4 kJ mol^{-1}, and −48 ± 1 J K^{-1} mol^{-1} for the bromo-complex respectively.

THE rates of aquation of $[CoX(NRH_2)(en)_2]^{2+}$ ($X = Cl$ or Br^-; en = ethylenediamine; R = alkyl group) are acid independent below pH 3. On the other hand, the pseudo-first-order rate constants of aquation of the corresponding complexes of aromatic amines exhibit an inverse first-order dependence in $[H^+]$ at *ca.* pH 2.[1,2] This effect was attributed to the operation of a conjugate-base mechanism in the aquation reactions of the latter complexes, in which it was postulated that the NH proton of the co-ordinated aromatic amine undergoes dissociation to generate a reactive conjugate base. However, the p*K* values of the NH groups in such complexes have not been determined.

Imidazole is known to be a weak acid.[3] It is also fairly well established that this ligand co-ordinates to metal ions through the tertiary nitrogen atom.[3-7] It is, however, not known to what extent this biologically important ligand and its imido-base labilize the co-ordination sphere of the metal ions in their complexes. It was, therefore, considered worthwhile to prepare some imidazole (imH) complexes of Co^{III} and to study their reactivities in acidic and basic media. We report in this paper the kinetics of acid and base hydrolysis of $[CoX(imH)(en)_2]^{2+}$ cations ($X = Cl$ or Br). The aim of this work is to examine the effect of co-ordination on the acidity of imidazole and the labilizing action of imidazole and its conjugate base on the Co–X bond. In order to understand the mechanism of aquation of $[CoX(imH)(en)_2]^{2+}$ we have also investigated the mercury(II)- and sulphate-catalysed aquation of these complexes.

EXPERIMENTAL

The chlorobis(ethylenediamine)(imidazole)cobalt(III) chloride and bromobis(ethylenediamine)(imidazole)cobalt(III) bromide were prepared by the method of Bailar and Clapp.[8] The crude products were recrystallized twice from aqueous hydrochloric or hydrobromic acid solutions. Repeated crystallization of the halide salts from aqueous perchloric acid solutions yielded the perchlorate salts which were washed successively with ice-cold water, ethanol, and diethyl ether and finally stored over fused calcium chloride {Found: Cl, 7.3; Co, 12.0. Calc. for $[CoCl(imH)(en)_2][ClO_4]_2$: Cl, 7.4; Co, 12.2. Found: Br, 15.3; Co, 11.2. Calc. for $[CoBr(imH)(en)_2][ClO_4]_2$: Br, 15.2; Co, 11.2%}.

The spectral measurements were made on Beckmann DU 2 and Perkin-Elmer 337 spectrophotometers. Sodium perchlorate (Riedel) was used for the ionic strength adjustment. Imidazole (Fluka A.G.) was used without further purification. Buffer mixtures were prepared from AnalaR grade sodium hydroxide and acetic acid. Dowex 50W-X8 resin in the acid form was used for ion-exchange experiments.

Kinetics.—The rates of aquation of the complexes at different pH and sulphate concentration were followed by potentiometric titration of halide ion after subjecting the reaction mixture at known time intervals to cation exchange as described earlier.[9] The base hydrolysis and mercury(II)-catalysed aquation reactions were studied spectrophoto-

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metrically. The reaction mixture, prepared by rapidly mixing the thermostatted components, was quickly transferred to a 10-mm quartz cell kept in the thermostatted compartment of the spectrophotometer. The decrease in absorbance at the preset wavelengths (see Tables 4 and 5) was followed with time. The pseudo-first-order rate constants ($k_{obs.}$) were computed from the gradients of plots of $\ln(V_\infty - V_t)$ or $\ln(D_t - D_\infty)$ against time where the terms have their usual meaning.[9] The error in individual $k_{obs.}$ values was obtained from the standard deviation of the gradient of the kinetic plot; $k_{obs.}$ was weighted inversely as its variance when calculating its average from replicate runs. All the calculations were made by means of a least-squares computer program on an IBM 1130 computer.

RESULTS

The chlorobis(ethylenediamine)(imidazole)cobalt(III) cation had absorption maxima at 365 and 535 nm with molar absorption coefficients of 94.1 and 77.8 dm^3 mol^{-1} cm^{-1} respectively in 0.10 mol dm^{-3} $HClO_4$. The corresponding bromo-complex exhibited only one band centred at 546 nm ($\varepsilon_{max.}$ 85.0 dm^3 mol^{-1} cm^{-1} in 0.10 mol dm^{-3} $HClO_4$) with strong absorption at *ca.* 330 nm. The spectral data for $[CoCl(imH)(en)_2]^{2+}$ are in satisfactory agreement with those of the analogous complexes of pyridine, and of benzylamine recently reported by Kindred and House [10] which was synthesized by the method of Bailar and Clapp [8] and established to be the *cis* isomer. Considering the method of preparation and the spectral data, the complexes are assigned the *cis* configuration. The i.r. spectra of both the bromo- and chloro-complexes in Nujol mulls are similar in the range 400—4 000 cm^{-1} with bands at 876 and 895 cm^{-1} which may be taken to be the components of the CH_2 rocking modes of ethylenediamine. However, assignment of the *cis* configuration [11,12] to the complexes on this basis is inconclusive as the spectrum of imidazole also has an absorption at 894 cm^{-1}. The spectra of the products of spontaneous and mercury(II)-catalysed aquation of both the complexes at pH 1 exhibited maxima at 343 ± 2 and 483 ± 2 nm with molar absorption coefficients of 81.6 ± 1.0 and 75.5 ± 1.0 dm^3 mol^{-1} cm^{-1} respectively. These data agree satisfactorily with the corresponding data for *cis*-$[Co(amine)(en)_2(OH_2)]^{3+}$ [amine = NH_3,[13] py, or $N(CH_2Ph)H_2$ [10]]. The product of base hydrolysis of the chloro-complex after acidification to pH 1 also exhibited the characteristic absorption of the aqua-complex generated by aquation. It is, therefore, believed that the aqua-product $[Co(imH)(en)_2(OH_2)]^{3+}$ exists predominantly in the *cis* form,[10] and imidazole is not lost from the cobalt centre in the aquation and base-hydrolysis reactions.

TABLE 1

Effect of pH on the acid hydrolysis of *cis*-$[CoCl(imH)(en)_2]^{2+}$ at $I = 0.3$ and [complex] = 4.8×10^{-3} mol dm^{-3}

θ_c [a] / °C	$[H^+]$ / mol dm^{-3}	$10^5k_{obs.}$ / s^{-1}	10^5k_1 / s^{-1}	$10^{11}k_2K_{NH}$ / mol dm^{-3} s^{-1}
50.0	0.010×10^{-1}	1.20 ± 0.05	1.21 ± 0.02	4.95 ± 0.11
	1.00	1.22 ± 0.03 [b]		
	3.00	1.12 ± 0.06		
	29.5×10^{-5}	1.25 ± 0.02 [b]		
	5.90	1.30 ± 0.04 [b]		
	2.95	1.43 ± 0.05		
	0.59	2.05 ± 0.03 [b]		
	0.295	2.85 ± 0.02 [b]		
55.0	0.010×10^{-1}	2.04 ± 0.05	2.04 ± 0.01	7.90 ± 0.20
	0.05	2.07 ± 0.03 [c]		
	1.00	2.05 ± 0.01 [b]		
	3.00	2.04 ± 0.02 [b]		
	29.0×10^{-5}	1.98 ± 0.04 [b]		
	5.80	2.15 ± 0.03 [b]		
	2.90	2.35 ± 0.02 [b]		
	0.58	3.36 ± 0.02 [b]		
	0.29	4.89 ± 0.08		
60.0	0.010×10^{-1}	3.45 ± 0.05	3.45 ± 0.02	12.8 ± 0.6
	1.00	3.46 ± 0.03 [b]		
	3.00	3.40 ± 0.07		
	28.5×10^{-5}	3.55 ± 0.10		
	5.7	3.66 ± 0.07		
	2.85	4.28 ± 0.14		
	0.57	5.65 ± 0.17		
	0.285	7.96 ± 0.18		

[a] ±0.1 °C. [b] Mean of duplicate runs. [c] Mean of single runs at I = 0.02, 0.06, and 0.22 mol dm^{-3}.

TABLE 2

Effect of pH on the acid hydrolysis if *cis*-$[CoBr(imH)(en)_2]^{2+}$ at $I = 0.3$ and [complex] = 2.0×10^{-3} mol dm^{-3}

θ_c [a] / °C	$[H^+]$ / mol dm^{-3}	$10^5k_{obs.}$ / s^{-1}	10^5k_1 / s^{-1}	$10^{11}k_2K_{NH}$ / mol dm^{-3} s^{-1}
50.0	0.010×10^{-1}	5.30 ± 0.12	5.52 ± 0.10	33.4 ± 0.7
	1.00	5.54 ± 0.10		
	3.00	5.67 ± 0.11		
	29.5×10^{-5}	5.49 ± 0.15		
	5.90	6.16 ± 0.12 [b]		
	2.95	6.67 ± 0.09 [c]		
	0.59	11.3 ± 0.1 [b]		
	0.295	17.2 ± 0.3 [d]		
55.0	0.010×10^{-1}	9.50 ± 0.14	9.57 ± 0.11	58.5 ± 1.6
	1.00	9.41 ± 0.15		
	3.00	9.78 ± 0.14		
	29.0×10^{-5}	9.92 ± 0.12		
	5.80	11.1 ± 0.1		
	2.90	11.7 ± 0.2		
	0.58	19.3 ± 0.4		
	0.29	29.7 ± 0.3		
60.0	0.010×10^{-1}	16.3 ± 0.4	16.4 ± 0.7	107 ± 2
	1.00	17.3 ± 0.3		
	3.00	15.0 ± 0.4		
	28.5×10^{-5}	16.6 ± 0.4		
	5.70	18.8 ± 0.6		
	2.85	21.1 ± 0.6 [d]		
	0.57	34.7 ± 0.3		
	0.285	54.4 ± 1.0 [b]		

[a] ±0.1 °C. [b] Mean of duplicate runs. [c] Mean of seven runs at $[Na(O_2CMe)]$ = 0.01—0.1 mol dm^{-3}. [d] Mean of triplicate runs.

Aquation.—The aquation of the complexes was studied in $HClO_4$ and acetate-buffer media. Adjustment of acidity in the range $[H^+] = 0.001 - 0.3$ mol dm^{-3} was made with perchloric acid. The $[H^+]$ values of the buffer medium were calculated by taking the dissociation constant of acetic acid to be 2.95×10^{-5}, 2.90×10^{-5}, and 2.85×10^{-5} mol dm^{-3} at 50, 55, and 60 °C (I = 0.3 mol dm^{-3}) respectively.[14] Values of $k_{obs.}$ at constant pH were virtually independent of acetate-ion concentration in the range 0.01—0.1 mol dm^{-3}. The rate data (Tables 1 and 2) are consistent with the mechanism in equations (1)—(3) which

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gives rise to rate equation (4) Equation (4) reduces to (5) if $K_{\mathrm{NH}}[\mathrm{H}^+]^{-1} \ll 1$.

$$[\mathrm{CoX(imH)(en)_2}]^{2+} \overset{K_{\mathrm{NH}}}{\rightleftharpoons} [\mathrm{CoX(im)(en)_2}]^{+} + \mathrm{H}^+ \qquad (1)$$

$$[\mathrm{CoX(imH)(en)_2}]^{2+} + \mathrm{H_2O} \xrightarrow{k_1} [\mathrm{Co(imH)(en)_2(OH_2)}]^{3+} + \mathrm{X}^- \qquad (2)$$

$$[\mathrm{CoX(im)(en)_2}]^{+} + \mathrm{H_2O} \xrightarrow{k_2} [\mathrm{Co(im)(en)_2(OH_2)}]^{2+} + \mathrm{X}^- \qquad (3)$$

$$-\mathrm{dln}\,[\mathrm{Co^{III}}]/\mathrm{d}t = k_{\mathrm{obs.}} = \frac{k_1 + k_2K_{\mathrm{NH}}[\mathrm{H}^+]^{-1}}{1 + K_{\mathrm{NH}}[\mathrm{H}^+]^{-1}} \qquad (4)$$

$$k_{\mathrm{obs.}} = k_1 + k_2K_{\mathrm{NH}}[\mathrm{H}^+]^{-1} \qquad (5)$$

In accord with equation (5) plots of $k_{\mathrm{obs.}}$ against $[\mathrm{H}^+]^{-1}$ yielded excellent straight lines with positive gradients and intercepts. The intercepts of such plots strikingly coincided with the limiting value of $k_{\mathrm{obs.}}$ at $[\mathrm{H}^+] = 0.001$—0.3 mol dm^{-3}, indicating that the conjugate-base equilibrium becomes kinetically insignificant at pH *ca.* 3. The rate constant k_1 was, therefore, taken to be the weighted mean value of $k_{\mathrm{obs.}}$ at $[\mathrm{H}^+] = 0.001$—0.3 mol dm^{-3}; k_2K_{NH} was then calculated from equation (5) by a weighted least-squares procedure. The rate constant k_1 was independent of ionic strength and perchlorate concentration in the range 0.02—0.3 mol dm^{-3} (see footnote *b* of Table 1).

TABLE 3

Effect of sulphate ion on the aquation of $[\mathrm{CoX(imH)(en)_2}]^{2+}$ at $I = 0.3$, $[\mathrm{HClO_4}] = 0.001$, [complex] $= 3.9 \times 10^{-3}$—4.8×10^{-3} (X = Cl) and 2.0×10^{-3} mol dm^{-3} (X = Br)

$[\mathrm{Na_2SO_4}]$ / mol dm^{-3}	$10^5k_{\mathrm{obs.}}$ [a]/s^{-1} X = Cl$^-$ (60.0 ± 0.1 °C)	X = Br$^-$ (50.0 ± 0.1 °C)
0.01	3.75 ± 0.15	6.24 ± 0.09
0.02	4.03 ± 0.05	7.29 ± 0.23
0.04	4.50 ± 0.05	8.64 ± 0.20
0.06	4.94 ± 0.06	9.63 ± 0.25
0.10	5.37 ± 0.10 [b]	11.8 ± 0.5
10^5k_{ip}/s^{-1}	8.09 ± 0.69	25.7 ± 0.6
K_{ip}/dm^3 mol^{-1}	7.5 ± 1.1	4.4 ± 1.4

[a] Mean of triplicate runs. [b] $I = 0.313$ mol dm^{-3}.

TABLE 4

Rate and activation parameters for the mercury(II)-catalysed aquation of $[\mathrm{CoX(imH)(en)_2}]^{2+}$ at $I = 0.3$, $[\mathrm{HClO_4}] = 0.1$, [complex] $= 1.5 \times 10^{-3}$ (X = Cl, 300 nm), and 4.6×10^{-5} mol dm^{-3} (X = Br, 270 nm)

$10^3[\mathrm{Hg(ClO_4)_2}]$ / mol dm^{-3}	θ_c [a] / °C	$10^4k_{\mathrm{obs.}}$ / s^{-1}	10^4k_{Hg} / dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}
(*a*) X = Cl					
30.0	30.5	10.43 ± 0.09 [b]	0.348 ± 0.003	68.4 ± 0.7	−48 ± 2
10.0	35.0	4.99 ± 0.04	0.529 ± 0.010		
20.0		10.8 ± 0.1			
30.0		15.3 ± 0.1			
40.0		21.8 ± 0.1 [c]			
30.0	39.5	23.4 ± 0.4 [b]	0.781 ± 0.014		
(*b*) X = Br					
0.50	30.5	62.3 ± 2.4 [b]	124 ± 5	53.4 ± 0.4	−48 ± 1
0.25	35.0	42.4 ± 0.3	171 ± 3		
0.50		90.8 ± 1.4			
1.00		164 ± 11			
0.25	39.5	58.6 ± 0.9 [b]	234 ± 4		

[a] ±0.2 °C. [b] Mean of triplicate runs. [c] Mean of duplicate runs.

Sulphate-ion Catalysis.—The rate of elimination of halide ion from $[\mathrm{CoX(imH)(en)_2}]^{2+}$ was studied as a function of sulphate concentration at $[\mathrm{HClO_4}] = 0.001$ and $I = 0.3$ mol dm^{-3}. Spectrophotometric analysis of the reaction mixture in the range 330—600 nm indicated that the product is $[\mathrm{Co(imH)(en)_2(OH_2)}]^{3+}$ rather than $[\mathrm{Co(imH)(en)_2(SO_4)}]^{+}$. Examination of the rate data in Table 3, however, shows that $[\mathrm{SO_4}]^{2-}$ accelerates the rate of aquation of the complexes. The quantity $(k_{\mathrm{obs.}} - k_1)/[\mathrm{SO_4}^{2-}]$ decreased with increasing $[\mathrm{SO_4}^{2-}]$. This is evidence for equilibrium pre-association of $[\mathrm{CoX(imH)(en)_2}]^{2+}$ with $[\mathrm{SO_4}]^{2-}$ followed by the aquation of the ion pair $[\mathrm{CoX(imH)(en)_2}]^{2+},[\mathrm{SO_4}]^{2-}$ at a characteristic rate. If k_{ip} and K_{ip} are the rate constant of aquation and equilibrium constant of formation of the ion pair respectively then $k_{\mathrm{obs.}} = (k_1 + k_{\mathrm{ip}}K_{\mathrm{ip}}[\mathrm{SO_4}^{2-}])/(1 + K_{\mathrm{ip}}[\mathrm{SO_4}^{2-}])$. This relation ignores the k_2 path. This is justified as the hydrogen-ion concentration (calculated taking 2.4×10^{-2} mol dm^{-3} as the dissociation constant of $[\mathrm{HSO_4}]^-$ at 60 °C and $I = 0.3$ mol dm^{-3}) [15] in sulphate media varies from 1.0×10^{-3} to 0.18×10^{-3} mol dm^{-3} at which $k_{\mathrm{obs.}}$ at $[\mathrm{SO_4}^{2-}] = 0$ attains the limiting value. The values of k_{ip} and K_{ip} given in Table 3 were obtained from the gradient and intercept of the least-squares best fit of $(k_{\mathrm{obs.}} - k_1)^{-1}$ against $[\mathrm{SO_4}^{2-}]^{-1}$ taking $[\mathrm{SO_4}^{2-}] = [\mathrm{SO_4}^{2-}]_{\mathrm{T}}$.

Mercury(II)*-induced aquation.*—Mercury(II)-catalysed aquation was studied at constant pH and ionic strength at 30, 35, and 39.5 °C. The rate law for the reaction is given by $-\mathrm{dln}[\mathrm{Co^{III}}]/\mathrm{d}t = k_{\mathrm{obs.}} = k_{\mathrm{Hg}}[\mathrm{Hg}^{2+}]$ where k_{Hg} is the second-order rate constant defined as in $[\mathrm{CoX(imH)(en)_2}]^{2+} + \mathrm{Hg}^{2+}(\mathrm{aq}) \xrightarrow{k_{\mathrm{Hg}}} [\mathrm{Co(imH)(en)_2(OH_2)}]^{3+} + [\mathrm{HgX}]^+$. Values of k_{Hg} and the associated activation parameters are in Table 4.

Base Hydrolysis.—Rate data for the base-hydrolysis reactions are in Table 5. For the chloro-complex, a plot of $k_{\mathrm{obs.}}$ against $[\mathrm{OH}^-]$ at $[\mathrm{OH}^-] = 0.001$—0.006 mol dm^{-3} was linear with a positive gradient and intercept. The $[\mathrm{OH}^-]$-independent rate constant is reconciled with k_2 [equation (3)] and the term k_3 of the rate expression $k_{\mathrm{obs.}} = k_2 + k_3[\mathrm{OH}^-]$ is due to base hydrolysis of $[\mathrm{CoCl(im)(en)_2}]^{+}$ which is believed to involve a conjugate-base mechanism arising out of the deprotonation of the NH group of ethylenedi-

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[15] W. L. Marshall and E. V. Jones, *J. Phys. Chem.*, 1966, **70**, 4028.

amine.* Values of k_2 and k_3 obtained as the least-squares intercept and gradient of the plot of $k_{obs.}$ against $[OH^-]$ are given in Table 5. The rate data for the bromo-complex measured in imidazole buffer (at $[OH^-]_{calc.} = 1.22 \times 10^{-6}$—$3.05 \times 10^{-4}$ mol dm^{-3}) satisfactorily fit equation (4) with $[H^+] = K_{imH_2}[imH_2^+]/[imH]$ where K_{imH_2} is the dissociation constant of monoprotonated imidazole. Taking $[imH_2^+] = [HClO_4]$, $[imH] = [imH]_T - [HClO_4]$, k_1 (extrapolated) $= 6.38 \times 10^{-6}$ s^{-1}, and $K_{imH_2} = 10.2 \times 10^{-8}$ mol dm^{-3} at 31.8 °C,† the rate data were fitted to equation (4) allowing k_2K_{NH} and K_{NH} to vary {the input values of these parameters were obtained from the plot of $(k_{obs.} - k_1)^{-1}$ against $[H^+]$} and minimizing $\Sigma[(k_{calc.} - k_{obs.})/\sigma(k_{obs.})]^2$ by means of a computer program on an IBM 1130 computer. The best values of k_2K_{NH} and K_{NH} reproduce the observed rate constants satisfactorily (see Table 5).

TABLE 5

Rate data for base hydrolysis of $[CoX(imH)(en)_2]^{2+}$ at 31.8 ± 0.4 °C and $I = 0.3$ mol dm^{-3}

X = Cl		X = Br		
$10^3[NaOH]$ / mol dm^{-3}	$10^2k_{obs.}$ [a] / s^{-1}	$10^3[HClO_4]$ / mol dm^{-3}	10^3k/s^{-1} obs.[b]	10^3k/s^{-1} calc.[c]
1.00	1.93 ± 0.02 [d]	1.00	8.63 ± 0.15	8.14
2.00	1.94 ± 0.10 [e]	2.00	5.18 ± 0.05	4.84
3.00	2.71 ± 0.10 [e]	4.00	2.70 ± 0.04	2.64
4.00	3.94 ± 0.27 [d]	5.00	2.06 ± 0.03	2.13
5.00	4.62 ± 0.31 [e]	10.00	0.99 ± 0.01	1.06
6.00	4.47 ± 0.25	20.00	0.48 ± 0.01	0.48
		0.100	18.9 ± 0.3	20.5
		0.200	16.4 ± 0.3	17.5
		0.400	15.2 ± 0.3	13.6
		0.600	12.6 ± 0.2	11.1
		0.800	10.3 ± 0.9	9.41
10^2k_2/s^{-1}	1.28 ± 0.17	$10^{11}k_2K_{NH}$/ mol dm^{-3} s^{-1}		1.25 ± 0.04
k_3/dm^3 mol^{-1} s^{-1}	5.09 ± 1.00	$10^{10}K_{NH}$/mol dm^{-3}		5.08 ± 0.43
		10^2k_2/s^{-1}		2.46 ± 0.22

[a] [complex] $= 8.17 \times 10^{-4}$ (300 nm) or 2.85×10^{-5} mol dm^{-3} (240 nm). [b] $[imidazole]_T = 0.10$; [complex] $= 2.85 \times 10^{-5}$ mol dm^{-3} (260 nm). [c] Calculated from equation (4). [d] Mean of triplicate runs. [e] Mean of duplicate runs.

We examined the effect of sulphate ion on the base hydrolysis of the chloro-complex. The total concentrations of the complex and hydroxide ion were fixed at 2.85×10^{-5} and 2.0×10^{-3} mol dm^{-3} respectively, and that of $[SO_4]^{2-}$ was varied in the range 0.02—0.10 mol dm^{-3}. The constant $k_{obs.}$ measured spectrophotometrically at 240 nm had an average value of $(2.24 \pm 0.15) \times 10^{-2}$ s^{-1} (at 31.8 °C, $I = 0.3$ mol dm^{-3}) which agreed satisfactorily with the corresponding value at $[SO_4^{2-}] = 0$ (see Table 5). Evidence for the formation of a reactive ion pair $[CoCl(im)(en)_2]^+$,$[SO_4]^{2-}$ similar to its imidazole counterpart is lacking.

DISCUSSION

The pK_{NH} of $[CoCl(imH)(en)_2]^{2+}$ calculated from the values of k_2K_{NH} and k_2 is 9.21 ± 0.07 at 31.8 °C and $I = 0.3$ mol dm^{-3}. The base-hydrolysis data for the bromo-complex also yield 9.29 ± 0.04 for that complex. These data are comparable to the value for imidazole in N-bonded $[Ru(NH_3)_5(imH)]^{3+}$ (pK_{NH} 8.9 ± 0.1) [16] and for aquacobalamin–imidazole or ferrimyoglobin–imidazole complexes (pK_{NH} 10.3, 25 °C and $I = 0$).[3,4] The pK_{NH} of free imidazole has been reported to be 14.4 at 25 °C ($I = 0$).[3] It is evident that the acid ionization of imidazole is *ca.* 10^5 times more favourable when it is co-ordinated to Co^{III} than when it is free.

The bromoimidazole complex aquates about five times faster than the corresponding chloro-complex in the acid-independent path $[k_1(Br)/k_1(Cl) = 4.8 \pm 0.1$ at 50—60 °C]. The observed order of reactivity is associated with the activation entropies [*i.e.* $T(\Delta S^‡)$ (Br − Cl) > $\Delta(\Delta H^‡)$ (Br − Cl)] which are negative for both the complexes (see Table 6) and decrease in the order in which the solvation entropies of the departing ligands decrease [$S^\ominus(X^-,aq) = 55.2$ and 80.7 J K^{-1} mol^{-1} for X = Cl and Br respectively].‡ From the values of k_1 at 50 °C collected in Table 6 it is evident that the labilizing action of imidazole on the Co–X bond is comparable to that of pyridine, although the former ligand (due to the pyrrole nitrogen which serves as an internal electron-donor substituent) is expected to be a better electron donor than the latter. Values of $\Delta H^‡$ and $\Delta S^‡$ for the k_1 path of the chloro-complexes of pyridine and imidazole are to some extent sensitive to the nature of the amine (see Table 6). The observed catalytic effect of sulphate ion ($k_{ip}/k_1 = 2.3 \pm 0.2$ at 60 °C and 4.6 ± 0.1 at 50 °C for the chloro- and bromo-complexes respectively) and lack of evidence for the formation of $[Co(imH)(en)_2(SO_4)]^+$ support the rate-limiting Co–X bond breaking in the k_1 path of the imidazole complexes.

TABLE 6

Rate and activation parameters for the aquation of *cis*-$[CoX(en)_2]^{2+}$

L	X	10^5k_1 (50 °C) / s^{-1}	$\Delta H^‡$ / kJ mol^{-1}	$\Delta S^‡$ / J K^{-1} mol^{-1}
py	Cl	1.46 ± 0.04,[a] 1.1 [b]	102 ± 1 [a]	−21 ± 5 [a]
imH	Cl	1.21 ± 0.02	92.3 ± 1.2 (81.6 ± 1.7) [c]	−54 ± 3 (−191 ± 5) [c]
imH	Br	5.52 ± 0.10	94.5 ± 0.3 (102 ± 3) [c]	−34 ± 1 (−113 ± 8) [c]

[a] $I = 0.1$ mol dm^{-3} ($[NO_3]^-$), ref. 12. [b] $I = 0.01$ mol dm^{-3} ($[ClO_4]^-$); F. Basolo, J. G. Bergmann, R. E. Meeker, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1956, **78**, 2676. [c] Calculated from the temperature dependence of k_2K_{NH}.

For the mercury(II)-catalysed aquation $k_{Hg}(Br)/k_{Hg}(Cl)$ is 330 ± 30 at 30—40 °C. The reactivity sequence, $k_{Hg}(Br) > k_{Hg}(Cl)$, parallels the thermodynamic stability of $[HgX]^+$ species.[17] The activation enthalpy for the bromo-complex is 15 kJ lower than that for the chloro-complex (see Table 4). The $[HgBr]^+$ species is also

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* pK_a Values of $[Co(en)_3]^{3+}$ and $[Co(NH_3)_5(NO_2)]^{2+}$ are 15.2 and 16.8 respectively; D. M. Goodall and M. J. Hardy, *J.C.S. Chem. Comm.*, 1975, 919.

† K_{imH_2} was calculated to be $(10.2 \pm 0.4) \times 10^{-8}$ mol dm^{-3} at 31.8 °C ($I = 0.15$ mol dm^{-3}) from the pK data of $[imH_2]^+$ (C. Tanford and M. L. Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 434) and values of (9.8 or 10.2) $\times 10^{-8}$ for the same did not alter the k_2K_{NH} and K_{NH} values significantly.

‡ Calculated from the data given in W. L. Latimer, 'Oxidation Potentials,' 2nd edn., Prentice–Hall, New Jersey, 1959, pp. 54 and 59 taking 1 cal = 4.184 J.

[16] R. J. Sundberg, R. F. Bryan, I. F. Taylor, and H. Taube, *J. Amer. Chem. Soc.*, 1974, **96**, 381.

[17] S. J. Aschroft and C. T. Mortimer, 'Thermochemistry of Transition Metal Ions,' Academic Press, New York, 1970, p. 268.

enthalpy-stabilized to the extent of *ca.* 19 kJ relative to $[HgCl]^+$.[17] These data are in accord with the formation of a halide-bridged binuclear complex, $[(en)_2(imH)CoXHg]^{4+}$, as the reactive species. The value of $\Delta S^\ddagger$ is virtually independent of the nature of the halogen and the value of -48 J K^{-1} mol^{-1} (see Table 4) presumably indicates that steric change at the cobalt(III) centre *in the* dissociative transition state of the mercury(II)-catalysed reaction is not significant. It is of interest to note that mercury(II)-catalysed aquation of *cis*-$[CoCl(amine)(en)_2]^{2+}$ [amine = $NPhH_2$, py, and $N(CH_2Ph)H_2$] has been reported by Kindred and House[10] to generate the *cis*-aqua-products.

The chloro- and bromo-imidazole(1−) complexes, $[CoX(im)(en)_2]^+$, undergo first-order halide elimination with rate constants (k_2) of $(1.28 \pm 0.17) \times 10^{-2}$ and $(2.46 \pm 0.22) \times 10^{-2}$ s^{-1} at 31.8 °C respectively. The relative reactivities of the imidazole and imidazole(1−) complexes ($k_2/k_1 = 9.3 \times 10^3$ and 3.8×10^3 at 31.8 °C for the chloro- and bromo-complexes respectively) indicate that the labilizing action of im$^-$ on the Co–X bond is *ca.* 10^3 times stronger than that of its conjugate acid. It is, however, interesting to note that the aquation and base-hydrolysis rate constants of *cis*-$[CoCl(en)_2(OH)]^+$ [k(aquation) = 2.8×10^{-2} s^{-1}, k(base hydrolysis) = 22.9 dm^3 mol^{-1} s^{-1} at 31.8 °C][18] are comparable to the analogous parameters (k_2, k_3) for $[CoCl(im)(en)_2]^+$ (see Table 5). Apparently the labilizing action of im$^-$ on the Co–Cl bond is comparable to that of $[OH]^-$ when both these ligands are disposed *cis* to the chloride in $[CoClL(en)_2]^+$ (L = OH or im) complexes.

The overall activation entropy, $\Delta S^\ddagger$ (k_2K_{NH}), is highly negative for both the complexes (see Table 6). This, we believe, is not due to a large negative value for $\Delta S^\ddagger$(K_{NH}) as ΔS for N–H dissociation of free and monoprotonated imidazole as well as for imidazole co-ordinated to Co^{III} and Fe^{III} (in aquacobalamin–imidazole and ferrimyoglobin–imidazole complexes which carry 2+ and 1+ charges at the metal centre respectively) are −29, −25, −50, and −37 J K^{-1} mol^{-1} (25 °C, $I = 0$)[3,4] respectively. The values of $\Delta S^\ddagger(k_2K_{NH})$ indicate that the entropy of activation for the k_2 path is less than or comparable to that for the k_1 path. On this basis, and following the arguments of Tobe,[19] the steric change in the dissociative transition state of the k_2 path appears to be less likely.

[6/1079 *Received, 7th June,* 1976]

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[18] F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, pp. 171 and 181.

[19] M. L. Tobe, *Inorg. Chem.*, 1968, **7**, 1260.