Kinetics and Mechanism of Hydrolysis of *cis*-Benzimidazolechlorobis(ethylenediamine)cobalt(III) and *cis*-Benzimidazolebromobis(ethylenediamine)cobalt(III) Cations

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The kinetics of hydrolysis of *cis*-$[CoX(bzmH)(en)_2]^{2+}$ (X = Cl or Br; bzmH = benzimidazole; en = ethylenediamine) cations have been investigated in perchlorate medium of I = 0.3 mol dm^{-3} and at 20—60 °C. In the range pH 6.8—8.5 and 20—40 °C the rate law for aquation takes the form $-d\ln[Co^{III}]/dt = (k_1 + k_2K_{NH}[H^+]^{-1})/(1 + K_{NH}[H^+]^{-1})$ where k_1 and k_2 are the aquation rate constants of $[CoX(bzmH)(en)_2]^{2+}$ and $[CoX(bzm)(en)_2]^+$ respectively and K_{NH} is the acid-dissociation constant of the co-ordinated benzimidazole. The pK_{NH} of benzimidazole in $[CoCl(bzmH)(en)_2]^{2+}$ is 8.6 at 25 °C and I = 0.3 mol dm^{-3} from pH-titration and spectrophotometric measurements. Co-ordinated benzimidazole is 10^4 times stronger as an acid than free benzimidazole. The labilizing action of benzimidazole on the Co–X bond is stronger than that of imidazole in the k_1 path. This effect is, however, reversed in the k_2 path [*i.e.* k_2(im) > k_2(bzm)]. The imido-base $[CoX(bzm)(en)_2]^+$ labilizes the Co–X bond *ca.* 700 times stronger than its conjugate-acid analogue.

We recently reported the kinetics of acid and base hydrolysis of *cis*-$[CoX(imH)(en)_2]^{2+}$ (X = Cl or Br; imH = imidazole; en = ethylenediamine).[1] It was found that the acid strength of imidazole increases by a factor of *ca.* 10^5 on co-ordination to cobalt(III) and the imido-complex, *cis*-$[CoX(im)(en)_2]^+$, is *ca.* 10^3 times more reactive than its conjugate acid analogue. This difference in the labilities of *cis*-$[CoX(imH)(en)_2]^{2+}$ and *cis*-$[CoX(im)(en)_2]^+$ may be attributed to the combined effects of the overall charges of the complexes and the steric and electron-displacement properties of imH and its conjugate base which are, however, difficult to separate. It was, therefore, considered worthwhile to make a systematic investigation of the kinetics of hydrolysis of the corresponding substituted imidazole complexes which may be useful for understanding the factors affecting the labilizing action of imidazole and its conjugate base on the Co–X bond. The kinetic data may also be useful in estimating the effect of co-ordination on the pK_{NH} of substituted imidazole. With these aims, we have investigated the kinetics of hydrolysis of *cis*-[CoX-

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[1] A. C. Dash and S. K. Mohapatra, *J.C.S. Dalton*, 1977, 246.

$(bzmH)(en)_2]^{2+}$ (bzmH = benzimidazole, X = Cl or Br) cations.

EXPERIMENTAL

*Benzimidazole*chlorobis(ethylenediamine)cobalt(III) chloride and benzimidazolebromobis(ethylenediamine)cobalt(III) bromide were prepared by the method of Bailar and Clapp.[2] Repeated crystallization of the crude halide salts from aqueous perchloric acid solutions at 0 °C yielded the perchlorate salts which were washed successively with ice-cold water, ethanol, and diethyl ether and finally stored over fused calcium chloride in a desiccator painted black {Found: Cl, 6.3; Co, 10.7. Calc. for $[CoCl(bzmH)(en)_2][ClO_4]_2$: Cl, 6.7; Co, 11.1. Found: Br, 13.5, Co, 10.1. Calc. for $[CoBr(bzmH)(en)_2][ClO_4]_2$: Br, 13.8; Co, 10.2%}. Sodium perchlorate (Riedel) was used for ionic-strength adjustment. Benzimidazole was synthesized and purified by the published method.[3] Imidazole (Fluka, A.G.) was used without further purification. Sodium hydroxide, perchloric acid, and acetic acid were AnalaR grade chemicals. Dowex 50W-X8 resin in the acid form was used for ion-exchange experiments. Spectral measurements were made with Beckman DU2 and Perkin–Elmer 337 spectrophotometers. The i.r. spectra were recorded in Nujol mulls. pH-Titration curves were obtained by using a direct-reading Philips model 9040 pH meter equipped with glass and saturated-calomel electrodes. The meter was standardized against buffers of pH 4.0, 7.0, and 9.2.

TABLE 1

pK_{NH} of benzimidazolechlorobis(ethylenediamine)cobalt(III). $[complex]_T = 2.11 \times 10^{-4}$, $[imidazole]_T = 0.025$, and $I = 0.3$ mol dm^{-3}

$10^3[HClO_4]_T$ / mol dm^{-3}	$\varepsilon_{obs.}$ * / dm^3 mol^{-1} cm^{-1}	$10^3(\varepsilon_2 - \varepsilon_1)^{-1}$ / dm^{-3} mol cm	$10^{-6}[(\varepsilon_2 - \varepsilon_1)K_{NH}]^{-1}$ / cm	10^9K_{NH} / mol dm^{-3}
1.20	2 587	0.382 ± 0.077	0.162 ± 0.003	2.4 ± 0.4
2.83	2 147			
4.46	1 927			
5.54	1 877			
6.63	1 816			
8.80	1 754			

* At 285 nm and 25 °C; $\varepsilon_1 = 1\,612$ dm^3 mol^{-1} cm^{-1}.

Kinetics.—The rates of aquation of the complexes were studied in perchloric acid, acetate, and imidazole buffer media of $I = 0.3$ mol dm^{-3}. The concentration of the complexes was varied in the range 0.001—0.003 2 mol dm^{-3}. Solutions of desired compositions were prepared in flasks (50 cm^3) and thermostatted to ±0.1 °C. The reaction mixture (5 cm^3), withdrawn at convenient time intervals, was analyzed for the liberated halide potentiometrically using standard silver(I) nitrate (0.01—0.02 mol dm^{-3}) after removing the unchanged halogeno-complex and the aqua-product on Dowex 50W-X8 resin in the acid form. The reaction was followed to 60—90% completion. Pseudo-first-order rate constants ($k_{obs.}$) were obtained from the gradients of plots of $\ln(V_\infty - V_t)$ against time where V_∞ and V_t are the titres at time t and complete release of halide respectively. V_∞ was determined by subjecting the reaction mixture (5 cm^3) to base hydrolysis to ensure complete release of halide, acidifying the content, and then working up as mentioned above. The error in individual $k_{obs.}$ values (1—7%) 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 program on an IBM 1130 computer.

Determination of pK_{NH} *of* $[CoCl(bzmH)(en)_2]^{2+}$.—pH Titrations were performed at 25 °C. A stock solution (50 cm^3) of the chloro-complex with $[complex]_T = 3.24 \times 10^{-3}$ (or 2.10×10^{-3}), $[HClO_4] = 1.00 \times 10^{-3}$, and $I = 0.3$ mol dm^{-3} was titrated against 0.1 mol dm^{-3} alkali. A perchloric acid solution (50 cm^3) of $[H^+]_T = 1.00 \times 10^{-3}$ and $I = 0.3$ mol dm^{-3} was also titrated against 0.1 mol dm^{-3} alkali. Acid ionization of the co-ordinated benzimidazole was indicated at pH $\geqslant 6$.* Taking $pK_w = 14.0$ [4] and $f_{H^+} = f_{OH^-} = 0.76$ (where K_w and f stand for the thermodynamic ionic product of water and activity-coefficient factor respectively) the values of pK_{NH} (calculated from $\leqslant 30\%$ neutralization of the complex) were 8.4 ± 0.2 and 8.7 ± 0.1 when $[complex]_T = 3.24 \times 10^{-3}$ and 2.01×10^{-3} mol dm^{-3} respectively. Table 1 presents the molar absorp-

TABLE 2

Absorption data for chloro-, bromo-, and aqua-benzimidazolebis(ethylenediamine)cobalt(III) cations

Complex	$\lambda_{max.}$ / nm	ε [a] / dm^3 mol^{-1} cm^{-1}
$[CoCl(bzmH)(en)_2]^{2+}$	530	88.5
	520	82.2 [b]
	350 [c]	153
	265	8 993
	235	21 250
$[CoBr(bzmH)(en)_2]^{2+}$	540	85.0
	270 [c]	14 720
	255	19 320
$[Co(bzmH)(en)_2(OH_2)]^{3+}$	488	93.0 [d]
		93.6 [e]
		92.0 [f]
	480	96.6 [g]
		94.1 [h]
	270	7 160
		7 176

[a] All the molar absorption coefficients reported in this work were determined at pH (calc.) 1.0. [b] Ref. 7. [c] Shoulder. [d] The aqua-complex was generated by base hydrolysis of the chloro-complex in 0.01 mol dm^{-3} alkali followed by acidification with $HClO_4$. [e] The aqua-complex was generated by mercury(II)-catalysed aquation of the chloro-complex. [f] The aqua-complex was obtained from spontaneous aquation of the chloro-complex in 0.1 mol dm^{-3} $HClO_4$ at 60 °C. [g] Λ-*cis*-$[Co(bzmH)(en)_2(OH_2)]^{3+}$, ref. 7. [h] *cis,trans*-$[Co(bzmH)(en)_2(OH_2)]^{3+}$ mixture, ref. 7.

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* pK_{NH} values for $[Co(en)_3]^{3+}$ 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, 979.

[2] J. C. Bailar and L. B. Clapp, *J. Amer. Chem. Soc.*, 1945, **67**, 171.

[3] A. I. Vogel, 'A Text Book of Practical Organic Chemistry,' 3rd edn., Longmans Green and Co., 1957, p. 853.

[4] H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolytic Solutions,' 3rd edn., Reinhold, New York, 1958, p. 485.

tion coefficients ($\varepsilon_{obs.}$) of the chloro-complex at 285 nm and 25 °C in imidazole buffer at various [H$^+$]. It can be easily shown that the absorption data are related to K_{NH} [equation (1)] and [H$^+$] as $(\varepsilon_{obs.} - \varepsilon_1)^{-1} = (\varepsilon_2 - \varepsilon_1)^{-1} + [(\varepsilon_2 - \varepsilon_1)K_{NH}]^{-1}[H^+]$ where ε_1 and ε_2 are the molar absorption coefficients of $[CoCl(bzmH)(en)_2]^{2+}$ and $[CoCl(bzm)(en)_2]^+$ respectively. Taking K_{imH_2} (*i.e.* the dissociation constant of $[imH_2]^+$) as 7.59×10^{-8} mol dm^{-3},[5] $[imH_2^+] = [HClO_4]_T$, and $[imH] = [imH]_T - [HClO_4]_T$, the hydrogen-ion concentration of the buffer media was calculated from $[H^+] = K_{imH_2}[HClO_4]_T/([imH]_T - [HClO_4])$. A value of 8.6 ± 0.1 for pK_{NH} was then obtained from the gradient and intercept of a plot of $(\varepsilon_{obs.} - \varepsilon_1)^{-1}$ against [H$^+$].

RESULTS

The i.r. spectra of the chloro- and bromo-complexes display a strong band at 750 cm^{-1} which is also observed for benzimidazole. The presence of benzimidazole in these complexes is also indicated by the bands at 1 590, 1 550, and 1 540 cm^{-1}.[6] The u.v. and visible-spectral data for the chloro-, bromo-, and aqua-complexes are presented in Table 2. Fenemor and House[7] assigned the *cis* configuration to $[CoCl(bzmH)(en)_2]^{2+}$. Considering the method of preparation and the visible-spectral data it is reasonable to expect that the bromo-complex has also been isolated in the *cis* form.

TABLE 3

Rate data for aquation of *cis*-$[CoCl(bzmH)(en)_2]^{2+}$

pH [a]	$10^5k_{obs.}$/s^{-1}
30.0 °C	
7.03	9.50
7.20	15.5
7.39	21.4
7.63	36.0
7.78	46.5
7.84	48.0
7.98	65.3
8.12	77.9
8.30	93.3
35.0 °C	
6.93	22.9
7.11	30.3
7.30	44.4
7.53	67.0
7.69	93.7
7.74	107
7.89	128
8.02	158
8.21	200
40.0 °C	
0.52	0.84
1.00	0.85
3.00	0.99
4.52	1.21
4.99	1.47
5.21	1.90
6.85	39.6
7.03	60.4
7.22	87.5
7.45	140
7.60	188
7.66	203
7.80	259
7.94	285
8.13	384
45.0 °C	
0.52	1.80
1.00	1.89
3.00	1.94
4.52	2.54
4.82	3.30
5.22	4.49
50.0 °C	
0.52	3.01
1.00	3.20
3.00	3.24 ±0.10 [c]
3.53	3.42 ±0.10 [c]
4.23	3.76
4.53	4.39 ±0.02 [b]
5.01	7.48
5.23	9.38
5.43	12.8
5.53	14.4
55.0 °C	
0.52	5.87
1.00	5.93
3.00	6.21
3.54	6.15
4.23	7.74
4.54	8.33 ±0.18 [b]
5.01	15.2
5.24	16.9
5.44	25.4
5.54	30.3
60.0 °C	
0.52	10.6
1.00	10.4
3.00	10.7
3.55	11.8
4.24	13.3
4.55	15.3 ±0.2 [b]
5.02	23.4
5.25	32.9
5.45	47.4
5.55	54.9

[a] pH = $-\log[H^+]_{calc.}$. [b] Mean from at least triplicate runs at $[MeCO_2^-]$ = 0.01, 0.02, and 0.05 mol dm^{-3}; all the other rate constants are from a single run at each pH. [c] Mean from duplicate runs.

Aquation.—Rate data are collected in Tables 3 and 4. Perchloric acid was used to adjust the pH in the range *ca.* 0.52—3.0. The pH values (*ca.* 3.7—5.7) of acetate buffer media of definite composition were calculated from knowledge of the dissociation constant of acetic acid which varied from 3.05×10^{-5} to 2.84×10^{-5} mol dm^{-3} (*I* 0.3 mol dm^{-3}) in the range 30—60 °C.[8] 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 total concentration of imidazole in its buffer media was 0.10 or 0.15 mol dm^{-3}. Values of the acid-dissociation constant of $[imH_2]^+$ were taken to be 6.17×10^{-8}, 7.59×10^{-8}, 9.44×10^{-8}, 11.7×10^{-8}, and 14.1×10^{-8} mol dm^{-3} at 20, 25, 30, 35, and 40 °C respectively[5] to calculate the pH values of the imidazole buffer which varied from *ca.* 6.85 to 8.5. The rate data indicate that base hydrolysis of the complexes sets in above pH 3. It is, however, worth noting that $k_{obs.}$ exhibits a less than first-order dependence in $[H^+]^{-1}$ over the range pH 6.85—8.5 at which significant fractions of the complexes will exist as the imido-conjugate base, $[CoX(bzm)(en)_2]^+$. This shows that the base hydrolysis of the imido-conjugate base is not significant at pH $\leqslant 8.5$.

The rate data are consistent with the mechanism in equations (1)—(3) which give rise to rate equation (4). $k_{obs.}$ attains a constant value at pH 3.0. k_1 was, therefore, taken to be the weighted mean of $k_{obs.}$ at pH 0.52—3.0. In the range pH 3.7—5.7, a plot of $k_{obs.}$ against $[H^+]^{-1}$ was

$$[CoX(bzmH)(en)_2]^{2+} \overset{K_{NH}}{\rightleftharpoons} [CoX(bzm)(en)_2]^+ + H^+ \tag{1}$$

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

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

$$-\mathrm{d}\ln[Co^{III}]/\mathrm{d}t = k_{obs.} = \frac{k_1 + k_2K_{NH}[H^+]^{-1}}{1 + K_{NH}[H^+]^{-1}} \tag{4}$$

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[5] C. Tanford and M. L. Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 434.

[6] C. N. R. Rao, 'Chemical Applications of Infrared Spectroscopy,' 1st edn., Academic Press, New York, 1963, pp. 157, 324, 328.

[7] D. Fenemor and D. A. House, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1559.

[8] Ref. 4, p. 580.

linear in accordance with equation (5) {equation (4) reduces to (5) when $K_{\mathrm{NH}}[\mathrm{H}^+]^{-1} \ll 1$}. k_1 being known, k_2K_{NH} was

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

calculated from equation (5) by a weighted least-squares procedure utilizing the rate data in this range of pH at 45—60 °C for the chloro-complex and at 35—50 °C for the bromo-complex. With the extrapolated values of k_1 (see Table 5), all the other rate data were fitted to equation (4) allowing k_2K_{NH} and K_{NH} to vary {the input values of the parameters were obtained from a plot of $(k_{\mathrm{obs.}} - k_1)^{-1}$ against $[\mathrm{H}^+]$} and minimizing the sum of the weighted residuals. The reciprocal of the variance of $k_{\mathrm{obs.}}$ was taken to be the weighting factor.* The variance of k_1 was also taken into account when calculating k_2K_{NH} from equation (5). The calculated values of k_2K_{NH} and K_{NH} are given in Table 5.†

TABLE 4

Rate data for aquation of *cis*-$[\mathrm{CoBr(bzmH)(en)_2}]^{2+}$

pH [a]	$10^5k_{\mathrm{obs.}}/\mathrm{s}^{-1}$
20.0 °C	
7.21	15.9
7.80	55.9
7.96	84.4
8.16	123
8.30	152
8.50	181
25.0 °C	
7.12	33.4
7.72	120
7.87	154
8.07	198
8.21	273
8.40	340
30.0 °C	
0.52	1.47
1.00	1.80
3.00	1.65
4.51	1.84
4.81	2.04
5.21	2.64
7.03	65.7
7.20	103
7.39	122
7.63	204
7.78	249
7.84	314
7.98	325
8.12	423
8.30	583
35.0 °C	
0.52	2.74
1.00	3.11
	±0.10 [c]
3.00	2.87
4.51	3.33
4.82	3.84
5.21	5.43
40.0 °C	
0.52	5.17
	±0.14 [c]
1.00	5.34
3.00	5.44
	±0.20 [c]
3.52	5.52
4.22	5.98
	±0.13 [c]
4.52	6.42
	±0.11 [c]
4.99	8.51
5.22	10.5
5.42	13.5
5.52	13.8
45.0 °C	
0.52	10.5
	±0.3 [c]
1.00	10.0
3.00	10.2
4.22	12.1
4.52	13.3
5.22	24.2
5.43	32.4
5.52	38.4
	±3.5 [c]
50.0 °C	
0.52	19.9
1.00	19.4
3.00	20.6
	±0.7 [c]
3.53	21.0
4.23	23.5
	±2.2 [c]
4.53	26.4
	±0.2 [b]
5.01	48.8
5.23	53.8
5.43	79.3
5.53	98.1
	±4.2

[a–c] Same as in Table 3.

DISCUSSION

The values of $\mathrm{p}K_{\mathrm{NH}}$ of *cis*-$[\mathrm{CoCl(bzmH)(en)_2}]^{2+}$ and its bromo-analogue were found to be 8.6 ± 0.1 and 8.4 ± 0.1 (at 25 °C, $I = 0.3$ mol dm^{-3}) respectively. These data are *ca.* 1.2 pK units higher than for benzimidazole in N-bonded $[\mathrm{Ru(NH_3)_5(bzmH)}]^{3+}$ ($\mathrm{p}K_{\mathrm{NH}}$ 7.2 ± 0.1, I 0.003 mol dm^{-3}).[9] The $\mathrm{p}K_{\mathrm{NH}}$ of benzimidazole has been reported to be 12.3 [10] and 12.57 [11] at $I = 0.038\,5$ and 0.5 mol dm^{-3} (25 °C) respectively. The decrease in $\mathrm{p}K_{\mathrm{NH}}$ indicates the effect of co-ordination of benzimidazole to $\mathrm{Ru^{III}}$ and $\mathrm{Co^{III}}$. Disregarding the effect of X^- on the acid ionization of the co-ordinated benzimidazole, we obtained $\Delta H(K_{\mathrm{NH}}) = 41 \pm 4$ kJ mol^{-1} and $\Delta S(K_{\mathrm{NH}}) = -23 \pm 14$ J K^{-1} mol^{-1} from the temperature dependence of K_{NH} at 20—40 °C.

The rate and activation parameters for the aquation of *cis*-$[\mathrm{CoXL(en)_2}]^{2+}$ (L = bzmH or imH; X = Cl or Br) are collected in Table 6. It can be seen that the values of $k_1(\mathrm{bzmH})/k_1(\mathrm{imH})$ are 2.6 ± 0.1 and 3.6 ± 0.1 (50 °C) for X = Cl and Br respectively. The activation enthalpy (k_1 path) for the benzimidazole complex is, however, *ca.* 10 kJ mol^{-1} higher than for its imidazole counterpart. Presumably benzimidazole labilizes the Co–X bond to a greater extent than imidazole by exerting relatively stronger steric repulsion on the leaving halide ion. The sequence $k(\mathrm{Br}) > k(\mathrm{Cl})$ is valid for both k_1 and k_2 paths. The values of $[\Delta S^{\ddagger}(\mathrm{bzmH}) - \Delta S^{\ddagger}(\mathrm{imH})]$ for the k_1 path are 36 ± 8 and 47 ± 6 for the chloro- and bromo-complexes respectively. This probably indicates that benzimidazole sterically hinders the solvation of the tripositive cobalt(III) centre much more strongly than imidazole in the transition state of this path, which is predominantly dissociative in nature.

The value of k_2/k_1 is 7.5×10^2 (30 °C) for both the chloro- and bromo-benzimidazole complexes indicating that the labilizing action of bzm on the Co–X bond is much stronger than that of bzmH. This can be as-

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* The variance of $k_{\mathrm{obs.}}$ from a single run was taken to be the square of its least-squares standard deviation.

† Considering the base hydrolysis of the imido-complex, $[\mathrm{CoX(bzm)(en)_2}]^+ + \mathrm{OH}^- \xrightarrow{k_{\mathrm{B}}} [\mathrm{Co(bzm)(en)_2(OH)}]^+ + \mathrm{X}^-$, and the reactions (1)—(3), and using $[\mathrm{OH}^-] = K_{\mathrm{w}}/[\mathrm{H}^+]$, equation (4) will have the form: $k_{\mathrm{obs.}} = (k_1 + k_2K_{\mathrm{NH}}[\mathrm{H}^+]^{-1} + k_{\mathrm{B}}K_{\mathrm{NH}}K_{\mathrm{w}}[\mathrm{H}^+]^{-2})/(1 + K_{\mathrm{NH}}[\mathrm{H}^+]^{-1})$. Rate data when fitted to this form of $k_{\mathrm{obs.}}$ by varying k_2K_{NH}, $k_{\mathrm{B}}K_{\mathrm{NH}}$, and K_{NH} yielded unacceptable values of these parameters. For instance, we obtained $k_2K_{\mathrm{NH}} = (6.09 \pm 0.20) \times 10^{-11}$ s^{-1}, $k_{\mathrm{B}}K_{\mathrm{NH}} = (0.04 \pm 131) \times 10^{-8}$, and $K_{\mathrm{NH}} = (8.29 \pm 2.5) \times 10^{-9}$ mol dm^{-3} from the rate data of the chloro-complex at 40 °C using $k_1 = 0.88 \times 10^{-5}$ s^{-1} and $K_{\mathrm{w}} = 5.19 \times 10^{-14}$ mol^2 dm^{-6}.

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

[10] D. O. Jordan and H. F. W. Taylor, *J. Chem. Soc.*, 1946, 994.

[11] H. Walba and R. W. Isensee, *J. Amer. Chem. Soc.*, 1955, **77**, 5488.

cribed to the overall effects of the net charge of the complexes as well as to the electron-displacement properties of benzimidazole and benzimidazole(1—). It is, however, interesting to note that k_2(bzm)/k_2(im) (30 °C) = 0.15 and 0.4 for the chloro- and bromo-complexes respectively. The benzimidazole(1—) species is expected to be a much weaker electron donor than imidazole(1—) as the negative charge of the former can be delocalized on the benzene ring. Since the charge effect remains constant, the values of k_2(bzm)/k_2(im) indicate that k_2 parallels the electron-displacement behaviour of bzm and im towards the cobalt(III) centre. The relatively small steric effect of these ligands is, however, overshadowed by their electronic effects in the k_2 path.

TABLE 5

Calculated parameters from equation (4) for the aquation of *cis*-[CoX(bzmH)(en)$_2$]$^{2+}$

θ_c / °C	10^5k_1 / s^{-1}	$10^{11}k_2K_{NH}$ / mol dm^{-3} s^{-1}	10^9K_{NH} / mol dm^{-3}
(*a*) X = Cl			
30.0	0.25 *	0.97 ± 0.02	5.13 ± 0.37
35.0	0.48 *	2.63 ± 0.07	7.35 ± 0.57
40.0	0.88 ± 0.04	6.08 ± 0.13	8.44 ± 0.50
45.0	1.90 ± 0.04	16.6 ± 1.5	
50.0	3.16 ± 0.07	35.2 ± 1.1	
55.0	5.95 ± 0.08	71.7 ± 2.1	
60.0	10.6 ± 0.1	128 ± 2	
(*b*) X = Br			
20.0	0.30 *	1.08 ± 0.08	2.48 ± 0.54
25.0	0.63 *	2.68 ± 0.10	3.94 ± 0.55
30.0	1.64 ± 0.16	5.91 ± 0.27	5.83 ± 0.87
35.0	2.81 ± 0.08	15.9 ± 0.8	
40.0	5.33 ± 0.04	30.0 ± 1.2	
45.0	10.3 ± 0.1	83.4 ± 1.0	
50.0	19.8 ± 0.3	219 ± 11	

* Obtained from a plot of log k_1 against T^{-1}.

TABLE 6

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

L	X	10^5k_1 (50 °C) / s^{-1}	$\Delta H^‡$ / kJ mol^{-1}	$\Delta S^‡$ / J K^{-1} mol^{-1}	10^3k_2 (30 °C) / s^{-1}	$\Delta H^{‡\,a}$ / kJ mol^{-1}	$\Delta S^{‡\,a}$ / J K^{-1} mol^{-1}
bzmH	Cl	3.16 ± 0.07	101 ± 2 (133 ± 2) [b]	−18 ± 7 (−15 ± 8) [b]	1.88 ± 0.14	92 ± 5	8 ± 14
	Br	19.8 ± 0.3	106 ± 2 (135 ± 3) [b]	13 ± 5 (5 ± 10) [b]	10.1 ± 1.5	94 ± 5	28 ± 17
imH	Cl	1.21 ± 0.02	92.3 ± 1.2	−54 ± 3	12.8 ± 1.7 [c]		
	Br	5.52 ± 0.10	94.5 ± 0.3	−34 ± 1	24.6 ± 2.2 [c]		

[a] $\Delta H^‡(k_2) = \Delta H^‡(k_2K_{NH}) - \Delta H(K_{NH})$; $\Delta S^‡(k_2) = \Delta S^‡(k_2K_{NH}) - \Delta S(K_{NH})$. [b] Calculated from the temperature dependence of k_2K_{NH}. [c] At 31.8 °C, ref. 1.

Recently Fenemor and House[7] investigated the steric course of base hydrolysis of Λ-*cis*-[CoCl(bzmH)(en)$_2$]$^{2+}$ in 0.0167 mol dm^{-3} alkali. They reported that the product of base hydrolysis (at 25 °C) has the composition: 6% *trans*-[Co(bzmH)(en)$_2$(OH)]$^{2+}$, 52% *rac*-[Co(bzmH)(en)$_2$(OH)]$^{2+}$, and 68% Λ-*cis*-[Co(bzmH)(en)$_2$(OH)]$^{2+}$. The pK_{NH} value for *cis*-[CoCl(bzmH)(en)$_2$]$^{2+}$ indicates that the chloro-complex will exist exclusively as the imido-base, *cis*-[CoCl(bzm)(en)$_2$]$^+$, under the experimental conditions employed by Fenemor and House. As such the stereochemical results reported by them refer to the base hydrolysis of the imido-complex {*i.e.* [CoCl(bzm)(en)$_2$]$^+$ + [OH]$^-$ $\longrightarrow$ [Co(bzm)(en)$_2$(OH)]$^+$ + Cl$^-$} which presumably generates the trigonal-bipyramidal intermediates and consequently the rearranged products. It is, however, worth mentioning that the values of $\Delta S^‡$ for the stereoretentive[12] aquation of *cis*-[CoClL(en)$_2$]$^{n+}$ (n = 1 for L = OH, Cl, Br, NCS, N$_3$, and NO$_2$; n = 2 for L = amine) are either negative or low positive ($\Delta S^‡$ = +41.8 to −71 J K^{-1} mol^{-1}). This has been ascribed to the formation of a tetragonal-pyramidal transition state[12] in the aquation of such complexes. Since the activation entropies for k_1 and k_2 paths of benzimidazolehalogeno-complexes are negative and low positive respectively, it is quite likely that *cis*-[CoX(bzmH)(en)$_2$]$^{2+}$ and *cis*-[CoX(bzm)(en)$_2$]$^+$ pass through tetragonal-pyramidal transition states in the course of their aquation.

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