Base-catalysed Hydrolysis of *cis*-(Imidazolato)-, *cis*-(Benzimidazolato)- and *cis*-(*N*-Methylimidazole)-bis-(Ethylenediamine)halogenocobalt(III) Cations. A Comparison of the Reactivities of the Deprotonated Imidazole and Benzimidazole Complexes

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The base hydrolysis of the complexes *cis*-$[Co(en)_2B(X)]^{n+}$ [en = ethylenediamine; B = imidazole (Him), *N*-methylimidazole (mim), or benzimidazole (Hbzim); X = Cl or Br] has been investigated at 20–35 °C and $[OH^-]_T = (4.7–99.7) \times 10^{-3}$ mol dm^{-3} ($I = 0.10$ mol dm^{-3}) under which conditions the co-ordinated imidazole and benzimidazole undergo complete NH deprotonation. The activation parameters ($85 \leqslant \Delta H^‡/\text{kJ mol}^{-1} \leqslant 97$, $+84 \leqslant \Delta S^‡/\text{J K}^{-1}\text{ mol}^{-1} \leqslant +97$), and the rate dependence on the leaving groups and the non-labile amine ligands are consistent with a S_N1 CB mechanism. The electron-displacement properties of the N-co-ordinated imidazolate (im) and benzimidazolate (bzim) ions appear to enhance the pK_{NH} of the co-ordinated ethylenediamine, the effect being relatively more significant for the former anion. Analysis of the activation entropy data in terms of the dissociative activation model for the conjugate bases, *cis*-$[Co(en)(en - H)B(X)]^{n+}$ [B = im or bzim ($n = 0$); mim ($n = 1$)] indicates that the configurational rearrangement at the cobalt(III) centre most likely occurs in the transition state of the actual act of substitution for the less reactive chloro complexes. The presumed trigonal-bipyramidal intermediate is efficiently scavenged by azide.

Base hydrolysis of the complexes *cis*-$[Co(en)_2B(X)]^{2+}$ [en = ethylenediamine, B = imidazole (Him) or benzimidazole (Hbzim), X = Cl or Br] was investigated earlier[1–5] over a limited pH range at which cobalt(III)-promoted NH deprotonation of the imidazole and benzimidazole was evident. However, a systematic study reporting the rate and activation parameters for base hydrolysis of the conjugate bases of these complexes, *cis*-$[Co(en)_2(im/bzim)X]^+$, which might unravel some of the salient features of these imido base species with regard to NH deprotonation of the co-ordinated ethylenediamine, and the reactivities of the corresponding conjugate bases, has not yet appeared. Furthermore it would also be worthwhile to examine whether there exists any correlation between the activation entropy and the steric change in the base hydrolysis of *cis*-$[Co(en)_2B(Cl)]^{n+}$ [B = *N*-methylimidazole (mim) or bzim] reported by Fenemor and House.[6] We therefore undertook a study of the base hydrolysis of the complexes cited above including the corresponding mim complexes for which relevant data are also not available, under conditions at which the co-ordinated imidazole and benzimidazole are likely to undergo complete NH deprotonation.

Experimental

Preparation and Reagents.—The complexes, *cis*-$[Co(en)_2B(X)][ClO_4]_2$ (B = Him,[1] Hbzim[2] or mim;[7,8] X = Cl or Br) were prepared as described earlier and their purities checked by analysis of Co, halogen and ultraviolet-visible spectral data. All reagents were of Analar grade. The solutions were prepared in freshly prepared doubly distilled water, the second distillation being made from alkaline $KMnO_4$ in an all-glass still.

Kinetics.—The base hydrolysis reaction was followed spectrophotometrically using a fully automated HITECH (UK) SF 51 stopped-flow spectrophotometer equipped with a circulator (C-85D) and a cooler (FC-200). Equal volumes of prethermostatted complex and NaOH solutions, both adjusted to $I = 0.10$ mol dm^{-3} ($NaClO_4$), were mixed and the progress of the reaction was monitored at 240 (B = Him or min, X = Cl), 285 (B = Hbzim, X = Cl) or 340 nm (B = Him, Hbzim or mim, X = Br) at which there was a large absorbance decrease during the base hydrolysis of the complexes.

Runs were made under pseudo-first-order conditions with $[OH^-]_T/[\text{complex}]_T > 50:1$ and $[\text{complex}]_T = (5–60) \times 10^{-5}$ mol dm^{-3}. The decrease in absorbance with time for any run was displayed on the monitor of an Apple IIGS computer interface and was fitted by a single-exponential equation applicable to first-order kinetics with the help of a computer program from HITECH Scientific (UK). At least 10 runs were made at each $[OH^-]_T$ from which k_{obs} and its standard deviation were calculated.

The azide competition experiments in the base hydrolysis were conducted at 25 °C under pseudo-first-order conditions at constant $[NaOH]_T = 0.04$ mol dm^{-3} ($I = 1.0$ mol dm^{-3}) and varying $[NaN_3]_T$. The formation of the corresponding azido complexes, as indicated by the increase in absorbance with time during base hydrolysis, was monitored spectrophotometrically at 305 nm {$\varepsilon_{305} = 8040$ dm^3 mol^{-1} cm^{-1} for *cis*-$[Co(en)_2(Him)(N_3)]^{2+}$}[9] using the stopped-flow technique and the rate constants for the formation of the azido complex were determined in the usual manner.

Results and Discussion

The values of pK_{NH} for cobalt(III)-co-ordinated imidazole and benzimidazole are less than 11[1,4,9–11] and 9[2,5,12] respectively. Hence virtually complete NH deprotonation of these ligands in their complexes must occur under the conditions of the rate measurement. The constancy of the second-order rate constants (see Fig. 1 and Table 1) while supporting this assumption further suggests that the imido bases undergo hydrolysis exclusively *via* the base-catalysed path, *i.e.* the relatively slow background aquation of the imido base species[1,2,12] does not contribute significantly to the overall rate under the experimental conditions. Additional evidence in favour of the base-catalysed hydrolysis of the imido base species for the imidazole and benzimidazole complexes stems from the observed ionic strength dependence of the rate constant (see

Table 2) in accord with the theoretical relationship (1),[13] where

$$\log k_{OH} = \log k^0_{OH} + S_1[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})] \qquad (1)$$

$k^0_{OH} = k_{OH}$ at $I = 0$, $S_1 = 2\beta z_A z_B$ with $\beta = 0.51$, z_A and z_B denote the charges of the reacting species, *i.e.* the complex and OH^- ions respectively. The slopes of the weighted least-squares straight-line plots of log k_{OH} *versus* $I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ for the mim complexes are twice those of the corresponding imidazole and benzimidazole complexes, in full agreement with complete NH deprotonation of the co-ordinated imidazole and benzimidazole.

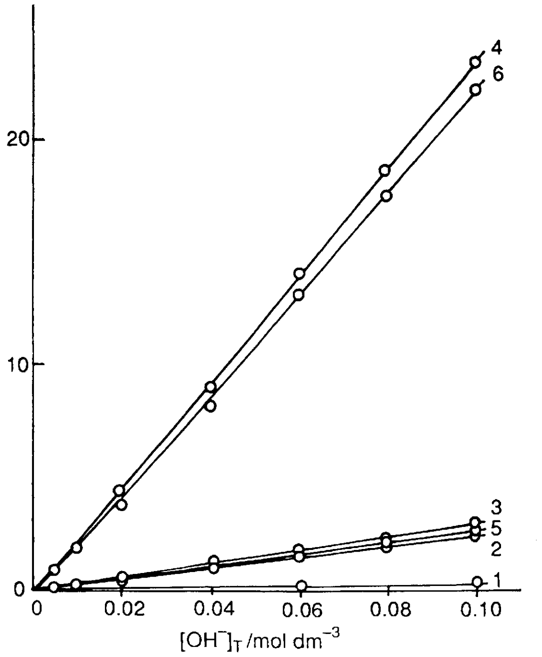

Fig. 1 Plots of k_{obs} *versus* $[OH^-]_T$ at 25 °C (I = 0.100 mol dm^{-3}) for the base hydrolysis of *cis*-$[Co(en)_2B(X)]^{n+}$: B/X$^-$ = im/Cl (1), im/Br (2), mim/Cl (3), mim/Br (4), bzim/Cl (5), bzim/Br (6)

Table 1 Rate data for base hydrolysis of *cis*-$[Co(en)_2B(X)]^{n+}$ at I = 0.100 mol dm^{-3},[a] [complex]$_T$ = (5–60) × 10^{-5} mol dm^{-3}

		k_{OH}[b]/dm^3 mol^{-1} s^{-1}			
B	X	20.0 ± 0.1	25.0 ± 0.1	30.0 ± 0.1	35.0 ± 0.1 °C
im	Cl	1.66 ± 0.05	3.50 ± 0.24	6.46 ± 0.14	11.9 ± 0.6
mim	Cl	14.0 ± 1.1	28.8 ± 2.0	51.4 ± 3.3	97.0 ± 7.4
bzim	Cl	13.3 ± 0.7	27.0 ± 1.5	48.3 ± 3.0	84.1 ± 5.9
im	Br	13.1 ± 0.7	25.9 ± 0.4	50.7 ± 1.3	90.8 ± 0.9
mim	Br	115 ± 9	233 ± 16	423 ± 34	780 ± 37
bzim	Br	106 ± 5	206 ± 14	356 ± 43	660 ± 46

[a] n = 2 for mim and 1 for im or bzim. [b] $k_{OH} = k_{obs}/[OH^-]$; k_{obs} values were determined at at least six $[OH^-]_T$ in the range (0.47–9.97) × 10^{-2} mol dm^{-3} with [NaOH] + [NaClO$_4$] = 0.100 mol dm^{-3}.

If we consider a general S_N1 CB mechanism as outlined in equation (2), then the observed pseudo-first-order (k_{obs}) and

$$\begin{array}{l} [Co(en)_2B(X)]^{n+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \\ \qquad [Co\{(en)_2 - H\}B(X)]^{(n-1)+} + H_2O \quad (2) \\ \qquad\qquad \Big\downarrow k_2 \\ \qquad\qquad \text{Product} \end{array}$$

second-order rate constants (k_{OH}), on the basis of the steady-state approximation for the amido conjugate base (due to NH deprotonation of the co-ordinated en), takes the form (3). In

$$k_{obs} = k_{OH}[OH^-] = \frac{k_1 k_2[OH]}{k_{-1} + k_2} \qquad (3)$$

equation (2) B = im or bzim (n = 1) and mim (n = 2). When the conjugate base formation is equilibrium controlled, *i.e.* $k_2 \ll k_{-1}$, $K_{cb} = k_1/k_{-1}$, equation (3) becomes (4).

$$k_{OH} = K_{cb}k_2 \qquad (4)$$

Values of k_{OH} at zero ionic strength (see Table 2) yield the relative reactivities of bromo and chloro complexes of the same charge type and for the same amine ligand: $(k^{Br}_{OH}/k^{Cl}_{OH})^0_B$ = 8.6 ± 0.5, 8.0 ± 0.5 and 7.3 ± 0.5 at 25 °C for B = im, mim and bzim respectively. These values are only marginally higher than the analogous data for aquation of the corresponding complexes [$(k^{Br}_{OH_2}/k^{Cl}_{OH_2})_B$ = 4, 5 and 5 for B = Him,[1,14] Hbzim[2,15] or bzim[2,12] at 25 °C]. However, comparatively higher values for the relative reactivities, $(k^{mim}_{OH}/k^{im}_{OH})^0_X$ = 14.0 ± 0.8 and 13.0 ± 0.6 for X = Cl and Br respectively (25 °C, I = 0), must be reconciled with the effect of the overall charges of the substrates and the relative electron-displacement properties of both the imidazolate (im) and mim ligands. These effects, however, influence the conjugate base equilibria and the

Table 2 Effect of ionic strength on the base hydrolysis of *cis*-$[Co(en)_2B(X)]^{2+}$ at 25 °C

I[a]/ mol dm^{-3}	k_{OH}/dm^3 mol^{-1} s^{-1}					
	B/X = Him/Cl	mim/Cl	Hbzim/Cl	Him/Br	mim/Br	HBzim/Br
0.020	—	—	—	36.6 ± 0.9	385 ± 12	—
0.040	3.99 ± 0.08	37.4 ± 1.1	30.2 ± 0.5	32.4 ± 0.9	286 ± 11	226 ± 6
0.050	—	—	—	29.6 ± 0.7	268 ± 3	—
0.060	3.75 ± 0.03	32.0 + 0.3	26.2 ± 0.3	—	—	209 ± 5
0.070	3.60 ± 0.08	28.9 ± 1.0	25.1 ± 0.4	—	—	191 ± 4
0.080	—	—	—	27.0 ± 0.7	233 ± 5	—
0.10	3.39 ± 0.02	25.7 ± 0.1	23.7 ± 0.6	24.9 ± 0.6	208 ± 3	181 ± 5
0.12	3.20 ± 0.04	23.6 ± 0.2	21.4 ± 0.5	—	—	167 ± 5
0.15	—	—	—	23.5 ± 0.3	172 ± 7	—
0.17	3.08 ± 0.08	21.3 ± 0.3	20.7 ± 0.6	—	—	—
0.20	—	—	—	21.7 ± 0.2	148 ± 2	—
0.22	2.39 ± 0.33	17.5 ± 0.2	18.5 ± 0.6	—	—	146 ± 3
log k^0_{OH}[b]	0.77 ± 0.01	1.91 ± 0.02	1.69 ± 0.03	1.69 ± 0.02	2.82 ± 0.02	2.55 ± 0.02
S_1[b]	−1.01 ± 0.06	−2.06 ± 0.09	−1.33 ± 0.12	−1.17 ± 0.06	−2.09 ± 0.06	−1.22 ± 0.08

[a] I = [NaOH] + [NaClO$_4$]. [b] See equation (1); correlation coefficient = 0.949–0.994 for plot of log k_{OH} *versus* $I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$; log k_{OH} was weighted inversely as its variance which was calculated from the variance of k_{OH}.

Table 3 Activation parameter data for the base hydrolysis of *cis*-$[Co(en)_2B(X)]^{n+}$ at $I = 0.100$ mol dm^{-3}

B	X	n[a]	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$\bar{S}^\circ(I^*) - \bar{S}^\circ(C)$/J K^{-1} mol^{-1}
im	Cl	1	96.9 ± 1.6	$+90 \pm 5$	$+24 \pm 5$
im	Br	1	93.4 ± 1.2	$+95 \pm 4$	$+4 \pm 4$
mim	Cl	2	93.2 ± 2.5	$+95 \pm 8$	$+29 \pm 8$
mim	Br	2	85.0 ± 1.5	$+84 \pm 5$	-7 ± 5
bzim	Cl	1	90.6 ± 2.7	$+86 \pm 9$	$+20 \pm 9$
bzim	Br	1	88.9 ± 1.5	$+97 \pm 5$	$+6 \pm 5$

[a] n = Charge of the substrate.

reactivities of the resulting conjugate bases in opposite directions. However, the reactivity sequence $k_{OH}^{mim} > 10\ k_{OH}^{im}$ (at $I = 0$, 25 °C) unambiguously suggested that the co-ordinated imidazolate anion enhanced the pK_{NH} of the co-ordinated en to a greater extent than did the co-ordinated mim ligand. This must be attributed to a relatively more favourable electron displacement *via* the Co–N σ bond for the co-ordinated imidazolate anion. This interpretation gains further support from a consideration of the relative reactivities of the imidazolate and benzimidazolate species *cis*-$[Co(en)_2(im/bzim)X]^+$ in the base-catalysed path as evident from the values of $(k_{OH}^{bzim}/k_{OH}^{im})_X^0 = 8.5 \pm 0.5$ and 7.2 ± 0.4 (25 °C, $I = 0$) for X = Cl and Br respectively; the relatively higher reactivities of the benzimidazolato species are attributed to the smaller pK_{NH}^{en} perburation due to the effective delocalisation of the negative charge of the benzimidazolate moiety over a large number of π centres of the aromatic ring. The relative steric effects of the Hbzim and Him ligands on the aquation rates of the corresponding complexes, *cis*-$[Co(en)_2B(Cl)]^{n+}$, are small $\{(k_{OH_2}^{Hbzim}/k_{OH_2}^{Him})_X = <3$ (X = Cl) < 5 (Br) (25 °C, $I = 0.010$ mol dm^{-3}),[1,2,14,15] $(k_{OH_2}^{Hbzim}/k_{OH_2}^{im})_X = \approx 0.1$(X = Cl), $\approx 0.3(Br^-)$[1,2,12] where $k_{OH_2}^{B}$ denotes the aquation rate constant of the species *cis*-$[Co(en)_2B(X)]^{n+}\}$.

The activation parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) collected in Table 3 are substantially larger than the values usually obtained when rate-limiting deprotonation of an amine proton[16–18] (*i.e.* $k_2 \gg k_{-1}$) or concerted amine-proton transfer (E_2 mechanism)[19] controls the rate of base hydrolysis of halogenoamine cobalt(III) complexes. Furthermore, no significantly different values of the activation parameters resulted upon varying the charge of the substrates as well as the steric and electronic displacement properties of the non-labile ligands; there was, however, a marked dependence of the rate on the nature of the leaving groups. Evidently the dissociation rate constants (k_2) of the conjugate bases [see equations (2) and (3)] have exceeded their reprotonation rate constant (k_{-1}) and the conventional dissociative conjugate base mechanism (S_N1 CB) prevailed.

The base hydrolysis of the substrates is reported by Fenemor and House[6] to be accompanied by appreciable steric change in the product due to intervention of five-co-ordinate trigonal-bipyramidal intermediates. If the configurational change takes place at least partly in the transition state of the dissociative process, this must lead to a considerable entropy gain for the transition state relative to the initial state of the conjugate bases, $[Co\{(en)_2 - H\}B(X)]^{(n-1)+}$. Using partial molar entropy values[20] of X^-(aq) and OH^-(aq) [$\bar{S}^\circ_{aq}(X) = 77.4, 91.2$ and 11.7 J K^{-1} mol^{-1} for X = Cl, Br and OH respectively at 298 K] the $\Delta S^\ddagger$ data were analysed on the basis of a conventional conjugate base mechanism [see equations (4) and (5)] assuming that the

$$\Delta S^\ddagger = \bar{S}^\circ(I^*) - \bar{S}^\circ(C) + \bar{S}^\circ(X^-) - \bar{S}^\circ(OH^-) \quad (5)$$

partial molar entropy of the dissociative transition state is the sum of that of the presumed five-co-ordinate intermediate, I* ($=[Co\{(en)_2 - H\}B]^{n+}$) and $\bar{S}^\circ(X^-)$, $\bar{S}^\circ(C)$ being the aqueous partial molar entropy of the substrate *cis*-$[Co(en)_2B(X)]^{n+}$. Interestingly, the calculated values of $\bar{S}^\circ(I^*) - \bar{S}^\circ(C)$ (see Table 3) were only small, positive or negative depending on the nature of the leaving groups, being negative or close to zero for the more reactive bromo complexes. This analysis shows that the entropy of the transition state is relatively higher than that of the initial state, for the chloro complexes. Thus the configurational change at the cobalt(III) centre observed in the product[6] might occur in the transition state[21] of the actual act of base hydrolysis, at least for the less reactive chloro complexes.

Azide Competition Experiments.—The formation of $[Co(en)_2(im)(N_3)]^+$ during the base hydrolysis of the corresponding halogeno complexes was evident (see Experimental section). At $[OH^-]_T = 0.04$, $[N_3^-]_T = 0$, 0.3 and 0.40 mol dm^{-3} ($I = 1.0$ mol dm^{-3}, 25 °C) values of k_{obs} are 0.072 ± 0.002, 0.074 ± 0.001 and 0.075 ± 0.005 s^{-1} for *cis*-$[Co(en)_2(im)Cl]^+$ and 0.556 ± 0.009, 0.63 ± 0.03 and 0.65 ± 0.03 for *cis*-$[Co(en)_2(im)Br]^+$ respectively, the rate data in the presence of N_3^- referring to the formation of the azido complex. Thus very efficient scavenging of the trigonal-bipyramidal intermediate by N_3^- is indicated. A similar trend was also indicated for the corresponding mim and Hbzim complexes but no quantitative assessment of the azide competition was attempted.

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