Base Hydrolysis of αβ-Nitro-, Azido- and Isothiocyanato-[1,9-bis(2′-pyridyl)-2,5,8-triazanonane]- and [1,11-Bis(2′-Pyridyl)-2,6,10-triazaundecane]-cobalt(III) Cations. Departure from First-order Hydroxide Dependence

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The rate law for the displacement of X^- from *syn*-αβ-$[Co(picdien)(NO_2)]^{2+}$ and *anti*-αβ-$[Co(picdien)(NCS)]^{2+}$ [picdien = 1,9-bis(2′-pyridyl)-2,5,8-triazanonane] by hydroxide in aqueous solution has been found to depart from the usual first-order dependence on $[OH^-]$ at $[OH^-] > 0.01$ mol dm^{-3}. Since there are three non-equivalent amine protons present, analysis of the data gives composite quantities, representing the sum of the three proton-transfer equilibrium constants, and the sum of the products of each of these equilibrium constants with the rate constant for the dissociation of the corresponding conjugate base. This is an example of *proton anomaly*, but while it is not possible to make an unambiguous assignment of equilibrium constant and rate constant for the formation and reaction of the most labile conjugate base, it is possible to set limits. The *anti*-αβ-$[Co(picdien)(N_3)]^{2+}$ cation and all the $[Co(picditn)X]^{2+}$ [picditn = 1,11-bis(2′-pyridyl)-2,6,10-triazaundecane] complexes examined, on the other hand, maintain a first-order dependence on $[OH^-]$ over the whole range of concentration studied.

Base-catalysed substitution reactions of cobalt(III) complexes have been shown to involve the deprotonation (frequently reversible) of a suitably sited amine group thereby generating a labile amido species that undergoes dissociatively activated substitution.[1] When the proton transfer is fast compared to the overall reaction rate and can be treated as a reversible pre-equilibrium, the rate equation for the reaction carried out under pseudo-first-order conditions ($[OH^-]$ is kept constant in any run) is $k_{obs.} = k_{OH}[OH^-]/(1 + K[OH^-])$ where $k_{obs.}$ is the pseudo-first-order rate constant. When only one type of amine proton is present in the complex, $k_{OH} = Kk_2$, where k_2 is the first-order rate constant for the dissociation of the conjugate base and K is the equilibrium constant for the reaction (1). In aqueous solution, $K = K_a/K_w$, where K_a is the acid dissociation constant for the amine complex and K_w the ionic product of water.

$$[L_4M(R_2NH)X]^{n+} + OH^- \rightleftharpoons [L_4M(R_2N)X]^{(n-1)+} + H_2O \quad (1)$$

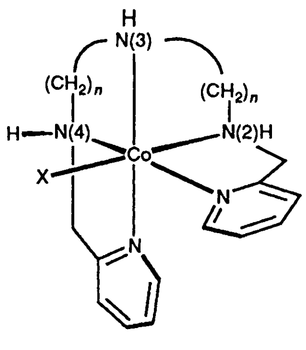
Usually K is too small, or k_2 too large, for it to be possible to study the reaction under conditions where $K[OH^-]$ is not small compared to 1 and, for this reason, the rate equation usually reduces to a simple first-order dependence on $[OH^-]$, $k_{obs.} = k_{OH}[OH^-]$. Under these circumstances, $k_{OH} = k_2K$ and it is not possible to separate the contributions from the acidity of the substrate (K) and the lability of the conjugate base (k_2). For this reason it is always of great interest to find a system where there is a departure from the simple first-order dependence upon $[OH^-]$ and, while such departures are not totally unknown, few, if any, arise from the conversion of a significant fraction of the substrate into the labile amido conjugate base. It is important to note that when the substrate contains non-equivalent sets of amine protons the same rate law will apply but the kinetics will reflect the removal of the most acidic proton, irrespective of whether the conjugate base thus formed is active or inactive. We have recently shown that complexes of the type *syn*- and *anti*-αβ-$[Co(L_5)X]^{2+}$ [L_5 = 1,9-bis(2′-pyridyl)-2,5,8-triazanonane (picdien) or 1,11-bis-(2′-pyridyl)-2,6,10-triazaundecane (picditn), X = Cl or Br] were unusually sensitive to base hydrolysis.[2] The search for the departure from a first-order dependence on $[OH^-]$ was unsuccessful and the rate of hydrolysis of the *anti*-αβ-$[Co(picdien)Cl]^{2+}$ cation was still first order in $[OH^-]$ at the highest rates that could be studied using the stopped-flow technique.[2] Consequently, an examination of the base hydrolysis of more tightly bound ligands was indicated in the hope that the smaller values of k_{OH} would allow the rate constants to be determined at hydroxide concentrations that were high enough for there to be a conversion of a major amount of the substrate into an amido conjugate base. The results are reported in this paper.

Experimental

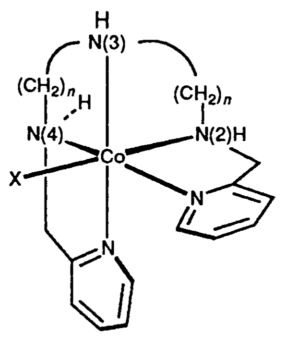
Reagents.—All the complexes used were samples whose preparation and characterisation has been reported elsewhere.[2] All other chemicals were AR reagents or else the best available. A fresh solution of 1.000 mol dm^{-3} sodium hydroxide (BDH) was used to prepare the stock hydroxide solutions. For the runs at $I = 1.00$ mol dm^{-3}, all dilutions were made with 1.000 mol dm^{-3} $NaClO_4$ made up by weight from AR $NaClO_4 \cdot H_2O$. For the runs at $I = 0.100$, a stock solution of 0.1000 mol dm^{-3} NaOH in water was prepared and all subsequent dilutions were performed with 0.1000 mol dm^{-3} $NaClO_4$.

Kinetics.—Well formed crystals that appeared to be identical to those used for the *X*-ray diffraction studies[3,4] were chosen under the microscope and used for the kinetic studies. These crystals dissolved only slowly in the appropriate $NaClO_4$ solution and needed to be crushed to hasten dissolution.

Preliminary studies of the spectra of the complexes before and after adding excess of sodium hydroxide were made with a Perkin-Elmer Lambda 5 spectrophotometer and the most favourable wavelengths chosen for the single-wavelength stopped-flow study. By working in the near-u.v. region it was possible to use very low concentrations of complex (5 × 10^{-5}



(1a)
αβ - *syn*



(1b)
αβ - *anti*

n = 2 picdien
n = 3 picditn

diluted to 2.5×10^{-5} mol dm^{-3}, except when the variable-ratio drive was used) and thereby ensure that [OH$^-$] was always in greater than 100-fold excess.

Freshly prepared stock solutions of the complex and sodium hydroxide of known concentration, both at the same ionic strength (usually 0.10 mol dm^{-3}, $NaClO_4$), were pre-thermostatted at the reaction temperature and mixed in a Hi-Tech SF3L stopped-flow spectrometer and the data were collected and processed with an ADS 1 data acquisition and analysis system. The equipment and details of the technique used to monitor the reaction have been reported elsewhere.[2] The first-order rate constants were determined by a non-linear least-squares regression to fit the curve of photon-multiplier (p.m.) voltage *versus* time. The concentrations of the solutions of the complexes were held low enough for the change in absorbance to be proportional to the change in % transmission, and hence the p.m. voltage. Experiments using a more elaborate and time-consuming data-processing program that converted the p.m. voltage into absorbance gave identical results.

Some of the runs were carried out using the variable-ratio drive that allowed the syringes to deliver their solutions in the ratio 1:2, 1:3, or 1:6 instead of the usual technique which delivered equal volumes. However, since the calibration was tedious this was only used in the region where the rate constants did not depend strongly upon [OH$^-$].

Results

Complexes and their Structure.—Although it was possible to isolate pure samples of the *syn* and *anti* αβ isomers (**1a**) and (**1b**) of the chloro and bromo picdien complexes, we have only been able to isolate one isomeric form of the nitro, azido, and isothiocyanato complexes, even though the ^{1}H n.m.r. spectra in $(CD_3)_2SO$ of impure samples indicate the presence of the other isomer. The ^{1}H n.m.r. spectra have been used to assign the configuration, which is *syn* for the nitro complex and *anti* for the rest.[2] The configuration of the nitro complex was confirmed by a single-crystal *X*-ray diffraction study some time ago.[4]

The low solubility of the picditn complexes in dimethyl sulphoxide (dmso) makes an n.m.r. study of the sort that was successful for the picdien complexes[2] unreliable. Single-crystal *X*-ray diffraction studies showed that the cation in $[Co(picditn)Cl][CoCl_4]\cdot 0.5H_2O$ had the *anti*-αβ configuration.[5] We have recently determined the structures of many of the other complexes used in this work by single-crystal *X*-ray diffraction. The azido and thiocyanato picdien species were confirmed as *anti*-αβ isomers, as was the thiocyanato picditn complex, both NCS complexes being N-bonded. In spite of much effort it was not possible to obtain suitable crystals of the 'nitro' picditn species.[3]

Kinetics.—The reaction between the complexes and OH$^-$ takes place in a single stage, first order in [complex], yielding $[Co(L_5)(OH)]^{2+}$. Acidification yields the aqua species which can be identified by comparison of its visible absorption spectrum with that of an authentic sample, but it is not possible to be sure whether it is the *syn* or *anti* form. Therefore, it is not possible to make any comment on the steric course of the base hydrolysis other than to say that the αβ geometry is retained throughout.

In the reactions between NaOH and the nitro picdien complex, studied at 360 nm, an immediate increase of absorbance was observed on mixing the reagents. This increase, which is complete in less than 0.5 ms, depended upon the concentration of hydroxide and could be as much as four-fold when [OH$^-$] = 0.10 mol dm^{-3}. Although it is tempting to speculate on the nature of this absorbance change, it would be premature to make further comment until it can be studied by a rapid-scan, stopped-flow spectrophotometer. Similar changes were not seen in the reactions of the other substrates.

For all the picdien complexes, including the chloro and bromo species, the displacement of X is followed by a slow, [OH$^-$]-dependent development of a deep blue coloration that is immediately destroyed on exposing the solution to air. The picditn complexes do not behave in this way. This change, possibly due to the formation of a complex of Co in a lower oxidation state, is of great interest to us and we are in the process of examining the occurrence, the nature, and the mechanism of this phenomenon and hope to report our conclusions eventually.

The subsequent reaction is too slow to interfere with the determination of the rate constant for the first step, $k_{obs.}$, the values of which are collected in Table 1. The rate constants for the base hydrolysis of the *syn*-αβ-nitro- and *anti*-αβ-isothiocyanato picdien complexes clearly become nearly independent of [OH$^-$] as the concentration approaches 0.10 mol dm^{-3}. Those for the other complexes studied do not show any departure from a first-order dependence on [OH$^-$] and a second set of runs at I = 1.0 mol dm^{-3} was carried out in order to investigate the effect of a ten-fold increase in [OH$^-$]. These rate constants are also reported in Table 1.

The temperature dependence of the rate constants was studied at a single hydroxide concentration (0.001 25 mol dm^{-3}) when the plot of $k_{obs.}$ *versus* [OH$^-$] was linear and at two hydroxide concentrations, 0.001 25 and 0.100 mol dm^{-3}, representing $K[OH^-] \ll 1$ and $K[OH^-] \gg 1$, respectively, when it was not. The data and the derived activation parameters are collected in Table 2.

Discussion

Plots of $k_{obs.}$ *versus* [OH$^-$] for the various picdien and picditn complexes are shown in the Figure. It is clear that, for the nitro and isothiocyanato picdien complexes, the relationship is far from linear and indeed the rate of reaction is almost independent of [OH$^-$] as the concentration approaches 0.10 mol dm^{-3}. The rates of hydrolysis of the azido complex, on the other hand, remain strictly first order with respect to [OH$^-$]. A second series of runs carried at I = 1.0 mol dm^{-3} with [OH$^-$] varying between 0.1 and 0.5 mol dm^{-3} also gave a linear relationship between $k_{obs.}$ and [OH$^-$] but with a reduced second-order rate constant. Similar treatment of the nitro and isothiocyanato picdien complexes showed that $k_{obs.}$ did not become any more independent of [OH$^-$] at the higher base concentrations. The saturation behaviour can be represented by the expression $k_{obs.} = ab[OH^-]/(1 + b[OH^-])$ and plots of

Table 1. Rate constants for the base-catalysed hydrolysis of αβ-$[Co(L_5)X]^{2+}$ [a]

Configuration	L_5	X	$[OH^-]$/mol dm^{-3}	$k_{obs.}$/s^{-1}
syn	picdien	NO_2	0.000 50	0.060 ± 0.001
			0.0050	0.72 ± 0.008
			0.0100	1.19 ± 0.02
			0.0200	1.82 ± 0.01
			0.0350	2.27 ± 0.03
			0.0500	2.88 ± 0.04
			0.0750	3.17 ± 0.05
			0.1000	3.33 ± 0.04
			0.0500[b]	1.64 ± 0.02
			0.0750[b]	2.00 ± 0.03
			0.1000[b]	2.38 ± 0.04
			0.200[b]	3.02 ± 0.03
			0.400[b]	3.64 ± 0.05
			0.500[b]	3.91 ± 0.05
anti	picdien	NCS	0.000 50	0.51 ± 0.008
			0.0050	5.3 ± 0.04
			0.0100	9.4 ± 0.1
			0.0200	15.0 ± 0.4
			0.0350	19.6 ± 0.3
			0.0500	22.9 ± 0.4
			0.0750	25.4 ± 0.4
			0.1000	27.3 ± 0.4
			0.0500[b]	12.6 ± 0.3
			0.0750[b]	16.4 ± 0.4
			0.1000[b]	19.6 ± 0.3
			0.200[b]	26.7 ± 0.5
			0.400[b]	31.9 ± 0.5
			0.500[b]	33.0 ± 0.5
anti	picdien	N_3	0.000 500	0.51 ± 0.006
			0.005 00	6.37 ± 0.08
			0.0100	12.7 ± 0.05
			0.0200	23.8 ± 0.1
			0.0350	45.5 ± 0.5
			0.0500	67 ± 0.8
			0.0750	91 ± 2
			0.100	111 ± 2
			0.0500[b]	19 ± 0.1
			0.0750[b]	29 ± 0.2
			0.100[b]	39 ± 0.3
			0.200[b]	71 ± 0.9
			0.400[b]	167 ± 3
			0.500[b]	200 ± 6
anti	picditn	NO_2	0.0050	23.5 ± 0.3
			0.0100	55 ± 0.8
			0.0200	106 ± 4
			0.0500	245 ± 4
anti	picditn	NCS	0.001 00	2.31 ± 0.04
			0.005 00	12.1 ± 0.05
			0.0100	24.3 ± 0.3
			0.0200	49.5 ± 0.7
			0.0350	78 ± 1.1
			0.500	109 ± 2
			0.750	168 ± 5
			0.100	255 ± 6
anti	picditn	N_3	0.001 25	4.19 ± 0.05
			0.002 50	8.97 ± 0.03
			0.005 00	18.2 ± 0.2
			0.0125	50.6 ± 0.6
			0.0250	98.0 ± 1.6
			0.0500	189 ± 4

[a] In water at 10 °C. I = 0.1 mol dm^{-3} ($NaClO_4$) except where otherwise indicated. [b] I = 1.00 mol dm^{-3} ($NaClO_4$).

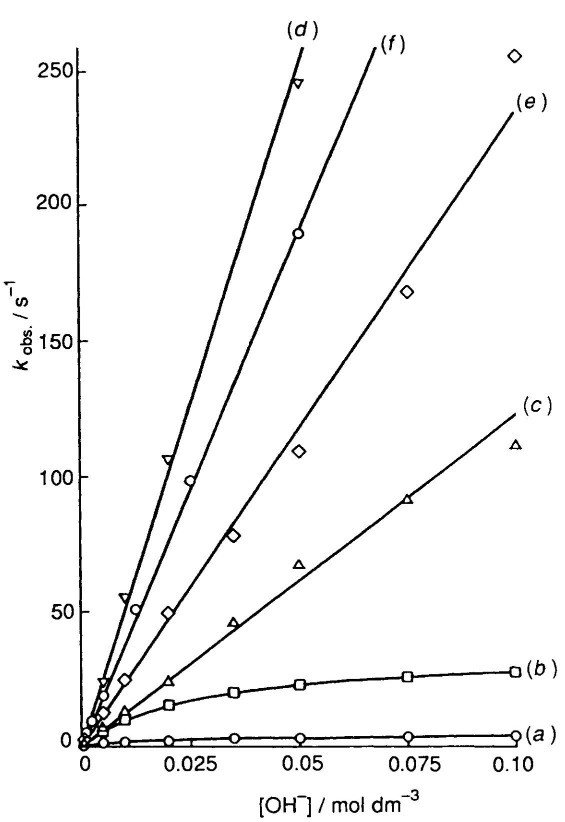


Figure. Plots of $k_{obs.}$ against $[OH^-]$ for the base hydrolysis of (*a*) *syn*-αβ-$[Co(picdien)(NO_2)]^{2+}$, (*b*) *anti*-αβ-$[Co(picdien)(NCS)]^{2+}$, (*c*) *anti*-αβ-$[Co(picdien)(N_3)]^{2+}$, (*d*) *anti*-αβ-$[Co(picditn)(NO_2)]^{2+}$, (*e*) *anti*-αβ-$[Co(picditn)(NCS)]^{2+}$, and (*f*) *anti*-αβ-$[Co(picditn)(N_3)]^{2+}$, in water at 10 °C, I = 0.10 mol dm^{-3} ($NaClO_4$)

$k_{obs.}^{-1}$ against $[OH^-]^{-1}$ are linear with slope = $(ab)^{-1}$ and intercept a^{-1}. Analysis showed that, while a was barely affected by the increase in ionic strength, the reduction in b due to the primary salt effect was just enough to cancel the effect of the increased $[OH^-]$, Table 3. Both the picditn complexes examined showed a linear dependence on $[OH^-]$ over the whole range of concentrations studied.

The base-catalysed substitution reactions of cobalt(III) amine complexes are usually characterised by a rate law of the form (2), and departures from this rate law are unusual and always of

$$-d[Co(L_5)X^{n+}]/dt = k_{OH}[Co(L_5)X^{n+}][OH^-] \quad (2)$$

considerable interest and they are seldom as marked as those found in the picdien system. The usual mechanism involves the removal, by hydroxide, of a suitably located amine proton to generate a dissociatively labile amido conjugate base. Most of the proton-transfer processes are reversible and frequently fast compared to the overall rate of base hydrolysis and under these circumstances the mechanism in which the conjugate base, formed by equilibrium (1) written above, followed by equations (3) and (4) gives the rate law (5), where $K = K_a/K_w$, the ratio of

$$[L_4Co(R_2N)X]^{(n-1)+} \xrightarrow{k_2} [L_4Co(R_2N)]^{n+} + X^- \quad (3)$$

$$[L_4Co(R_2N)]^{n+} + H_2O \xrightarrow{\text{fast}} [L_4Co(R_2NH)(OH)]^{n+} \quad (4)$$

$$-d[CoL_4(R_2NH)X^{n+}]/dt = k_2K[CoL_4(R_2NH)X^{n+}][OH^-]/(1 + K[OH^-]) \quad (5)$$

the acid dissociation constant of the complex and the ionic product of water. If $[OH^-]$ is held constant in any one run

Table 2. Temperature dependence of rate constants and activation parameters for the base hydrolysis of $[Co(L_5)X]^{2+}$ [a]

L^5	Isomer	X	Temp./°C	$k_{obs.}/s^{-1}$	$k_{OH}/dm^3\ mol^{-1}\ s^{-1}$	$\Delta H^{\ddagger}/kJ\ mol^{-1}$	$\Delta S^{\ddagger}/J\ K^{-1}\ mol^{-1}$
picdien	αβ-*syn*	NO_2	5.0	0.108 ± 0.002	86.5 ± 1.9	83.6 ± 0.6	93 ± 2
			10.0	0.204 ± 0.002	163 ± 2		
			15.0	0.392 ± 0.007	313 ± 5		
			20.2	0.721 ± 0.006	577 ± 5		
			25.1	1.29 ± 0.03	1 030 ± 20		
			30.1	2.25 ± 0.07	1 796 ± 55		
			35.1	4.17 ± 0.02	3 340 ± 11		
			5.0	1.76 ± 0.03[b]	—[c]	80.9 ± 0.5	52 ± 1
			10.0	3.44 ± 0.07[b]	—		
			15.0	6.45 ± 0.06[b]	—		
			20.0	11.61 ± 0.23[b]	—		
			25.0	21.0 ± 0.27[b]	—		
			30.0	35.5 ± 0.67[b]	—		
			35.0	61.6 ± 0.56[b]	—		
			40.0	109 ± 4[b]	—		
	αβ-*anti*	NCS	5.0	0.722 ± 0.017	578 ± 13	82.5 ± 1.3	105 ± 4
			10.0	1.39 ± 0.02	1 114 ± 17		
			15.0	2.74 ± 0.02	2 190 ± 16		
			20.0	4.76 ± 0.11	3 810 ± 88		
			25.0	8.48 ± 0.07	6 781 ± 52		
			5.0	14.4 ± 0.6[b]		81.2 ± 0.9	70 ± 3
			10.0	27.4 ± 0.4[b]			
			15.0	51.0 ± 0.7[b]			
			20.0	89.9 ± 1.6[b]			
			25.0	162 ± 2[b]			
			30.0	283 ± 11[b]			
	αβ-*anti*	N_3	5.0	0.869 ± 0.011	695 ± 8	76.1 ± 0.5	84 ± 2
			10.0	1.54 ± 0.014	1 235 ± 11		
			15.0	2.85 ± 0.05	2 281 ± 40		
			20.0	4.73 ± 0.06	3 780 ± 50		
			24.9	8.12 ± 0.07	6 490 ± 50		
			30.0	13.8 ± 0.2	11 020 ± 170		
			35.0	23.9 ± 0.4	19 120 ± 320		
picditn	αβ-*anti*	NO_2	5.0	3.55 ± 0.03	2 840 ± 24	80.5 ± 0.7	111 ± 2
			10.0	6.39 ± 0.04	5 112 ± 32		
			15.0	11.78 ± 0.04	9 424 ± 32		
			20.0	21.0 ± 0.4	16 800 ± 320		
			25.0	36.2 ± 0.3	28 960 ± 240		
			30.0	65.5 ± 0.4	52 400 ± 320		
			35.0	116.8 ± 0.7	93 440 ± 560		
			39.9	188.3 ± 5.2	150 640 ± 4 160		
	αβ-*anti*	NCS	5.0	1.59 ± 0.02	1 270 ± 16	85.3 ± 0.9	121 ± 3
			10.0	2.92 ± 0.04	2 340 ± 29		
			15.0	5.63 ± 0.08	4 500 ± 67		
			20.0	10.4 ± 0.2	8 310 ± 160		
			25.0	19.9 ± 0.3	15 900 ± 250		
			30.0	35.3 ± 0.6	28 300 ± 510		
	αβ-*anti*	N_3	5.0	2.41 ± 0.02	1 930 ± 16	70.4 ± 0.5	72 ± 1
			10.0	4.19 ± 0.05	3 350 ± 40		
			15.0	7.12 ± 0.08	5 700 ± 64		
			20.0	11.9 ± 0.1	9 520 ± 80		
			25.0	19.5 ± 0.25	15 600 ± 200		
			30.0	33.1 ± 0.5	26 400 ± 400		
			35.1	51.5 ± 0.4	41 200 ± 320		

[a] $[OH^-] = 1.25 \times 10^{-3}$ mol dm^{-3}, $I = 0.10$ mol dm^{-3} ($NaClO_4$). [b] $[OH^-] = 1.00 \times 10^{-1}$ mol dm^{-3}, $I = 0.10$ mol dm^{-3} (NaOH). [c] Rate constant essentially independent of $[OH^-]$ in this region.

to ensure pseudo-first-order conditions, $k_{obs.} = k_2K[OH^-]/(1 + K[OH^-])$. Usually $K[OH^-] \ll 1$ and the expression reduces to the usual second-order rate law, $k_{obs.} = k_2K[OH^-]$.

Although it is customary to discuss this reaction in terms of a unique amine proton, it should be realised that no examples with a single amine proton have yet been studied. The next simplest case would involve complexes with *n* equivalent protons but only one possible conjugate base, *e.g. trans*-$[Co(en)_2Cl_2]^+$ (en = ethylenediamine) or *trans*-*RSSR*-$[Co(cyclam)Cl_2]^+$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane) and then a statistical factor of *n* (taken up in *K*) is all that is required. However, the system becomes ambiguous when there is more than one potentially acidic proton, irrespective of whether or not the removal of the most acidic proton generates a labile conjugate base.

In a general case when there are *i* different possible acid–base equilibria, with equilibrium constant K_i and dissociation constant $k_2{}^i$ it can easily be shown that expression (7) applies.

$$k_{obs.} = \Sigma(k_2{}^iK_i)[OH^-]/(1 + \Sigma K_i[OH^-]) \qquad (7)$$

This has the same form as expression (6) for the simple reagents, but now $k_2K = \Sigma(k_2{}^iK_i)$ and $K = \Sigma K_i$ and as a result the

Table 3. Analysis of the $k_{obs.}$ *versus* $[OH^-]$ data according to the equation $k_{obs.} = k_{OH}[OH^-]/(1 + K'[OH^-])^a$ for the reaction $[Co(L_5)X]^{2+} + OH^- \longrightarrow [Co(L_5)(OH)]^{2+} + X^-$ in water at 10 °C

Isomer	L_5	X	k_{OH}/dm^3 mol^{-1} s^{-1}	k_2'/s^{-1}	K'/dm^3 mol^{-1}	10^{14} K'_a/mol dm^{-3}	pK_a
αβ-*syn*	picdien	NO_2	174 ± 9	3.97 ± 0.14^b	43.9 ± 0.5	35.0 ± 0.4	12.45
			51 ± 2	4.44 ± 0.12^b	11.5 ± 0.2	10.3 ± 0.1	12.99
αβ-*anti*		NCS	1 240 ± 12	36.2 ± 0.3^b	34.3 ± 0.3	27.0 ± 0.3	12.56
			364 ± 4	41.7 ± 0.6^c	8.7 ± 0.1	7.8 ± 0.1	13.11
αβ-*anti*		N_3	1 280 ± 12	> 1 500^b	< 0.85	<0.68	>14.17
			383 ± 4	> 2 500^c	< 0.15	<0.14	>14.87
αβ-*anti*	picditn	NO_2	4 660 ± 200	> 4 700^b	< 1.0	<0.8	>14.1
		NCS	2 440 ± 24	> 2 500^b	< 1.0	<0.8	>14.1
		N_3	3 794 ± 54	> 3 800^b	< 1.0	<0.8	>14.1

^{a} $k_{OH} = \Sigma(k_2{}^iK_i)$, $k_2' = \Sigma(k_2{}^iK_i)/\Sigma K_i$, and $K' = \Sigma K_i$. ^{b} I = 0.100 mol dm^3 (NaClO$_4$). ^{c} I = 1.000 mol dm^{-3} (NaClO$_4$).

intercept of the plot of $(k_{obs.})^{-1}$ against $[OH^-]^{-1}$ is no longer $1/k_2$ but takes the composite form $\Sigma K_i/\Sigma(k_2{}^iK_i)$ and the ratio of slope/intercept gives ΣK_i. A formal analysis of the consequences of this demonstrates the nature of the 'proton anomaly.'

Let K_x, K_y, K_z, . . ., *etc.* be the hydrolysis constants associated with the various amine protons and let $k_2{}^x$, $k_2{}^y$, $k_2{}^z$, . . ., *etc.* be the rate constants associated with the dissociation of the three corresponding conjugate bases, then $b = K_x + K_y + K_z + \ldots$, *etc.* and $a = (k_2{}^xK_x + k_2{}^yK_y + k_2{}^zK_z + \ldots$, *etc.*$)/(K_x + K_y + K_z + \ldots$, *etc.*). The following possibilities can then be considered.

(*i*) $K_x \gg K_y$, K_z, etc. *and* $k_2{}^x \gg k_2{}^y$, $k_2{}^z$, etc. That is, one amine group is much more acidic than the others and its deprotonation forms the activating amido group. Under these circumstances, the value obtained experimentally, $b = K_x$ and $a = k_2{}^x$, and a proper analysis of the system is possible.

(*ii*) $K_y \gg K_x$, K_z, etc., *but* $k_2{}^x \gg k_2{}^y$, $k_2{}^z$, etc. That is, one amine group is much more acidic than the others but the conjugate base formed on its deprotonation is not sufficiently reactive to contribute to the base hydrolysis. Under these circumstances $b = K_y$ and $a = k_2{}^xK_x/K_y$, *i.e.* $a \ll k_2$.

(*iii*) *Other cases.* It is not necessary to go through the individual combinations of possibilities because it is easy to see the consequence if two of the three proton-transfer equilibrium constants have similar magnitudes, much greater than the other, or indeed if all three have similar magnitudes. It will also follow that, except in case (*i*), *a* will always be less than the rate constant k_2 for the most labile conjugate base.

Thus, only one of the equilibrium constants K_i need be large enough for $K_i[OH^-]$ to be significant compared to 1 in order to get curvature in the plot of $k_{obs.}$ *versus* $[OH^-]$ and this need not be the one that is associated with the equilibrium that generates the active amido conjugate base. Indeed, if the acidity of the amine group arises from the stabilisation of its amido conjugate base by a delocalisation of the electron pair, the lability of the species with respect to ligand loss is likely to be reduced either because the bond with the leaving group is tightened, or because electron transfer towards the metal atom is inhibited. The departures from a first-order dependence on $[OH^-]$ observed in the base hydrolysis of $[Co(NH_3)_5\{OC(NH_2)_2\}]^{3+}$ [6] arise from the deprotonation of the urea. Since this is the leaving group, the conjugate base formed cannot be labile. It is possible that the departures from first order observed in the base hydrolysis of *cis*-$[Co(en)_2(Him)Cl]^{2+}$ (Him = imidazole) relate to deprotonation of the imidazole whereas the labilising amido group is a diaminoethane nitrogen.[7] Both of these systems fall into case (*ii*).

In the αβ-$[Co(picdien)X]^{2+}$ and αβ-$[Co(picditn)X]^{2+}$ complexes there are three non-equivalent protons. (The possible involvement of the pyridyl groups in some form of 'covalent hydration'[8] should not be ignored as this too could cause the observed saturation behaviour. However, it seems unlikely that the equilibrium constants associated with the addition of water across the $N{=}C$ bond and the subsequent deprotonation of the secondary amine nitrogen formed should be so dependent upon the nature of X, nor, indeed, upon the different sizes of the chelate rings of the picdien and picditn complexes.) The kinetics of proton exchange in the chloro, bromo, and nitro picdien cobalt(III) cations has been studied in acidified D_2O and preliminary results have been reported.[2] Rate constants for proton exchange have been assigned to each of the three amine protons and, under the conditions in which they were measured, can be equated to the appropriate k_1, the rate constant for deprotonation [the forward reaction in equilibrium (1)]. Comparison with k_{OH} gives limiting values for the ratio of k_{-1} [the rate constant for reprotonation, *i.e.* the reverse step in equilibrium (1)] to k_2. It was shown quite clearly that, although in the case of the bromo complex the system was approaching the point where $k_{-1} \approx k_2$, in the chloro system $k_{-1} > k_2$ and for the nitro complex $k_{-1} \gg k_2$. It is likely that the azido and thiocyanato complexes resemble the nitro species and so all three complexes and presumably their picditn analogues can be treated as cases where there is a pre-equilibrium proton transfer and $K_i = k_1{}^i/k_{-1}{}^i$.[2]

Plots of $(k_{obs.})^{-1}$ against $[OH^-]^{-1}$ are indeed linear and values of $\Sigma(k_2{}^iK_i)/\Sigma K_i$ and ΣK_i from these plots are collected in Table 3. Treatment of the data which show no departure from a first-order dependence on $[OH^-]$ simply yields a lower limit for $\Sigma(k_2{}^iK_i)/\Sigma K_i$ and an upper limit for ΣK_i, since the inverse plots pass through the origin, but their product ($=k_{OH}$) is defined quite precisely.

The temperature dependence of the rate constants has two significant features: (*i*) the plots of ln $(k_{obs.}/T)$ *versus* T^{-1} are linear and (*ii*) when there is saturation behaviour the slopes of the data at the low and high hydroxide concentrations are virtually identical. This suggests that ΔH° for the removal of the most acidic proton is very small. Both case (*i*) and case (*ii*) give $\Delta H_{obs.}{}^\ddagger = \Delta H_x{}^\ddagger + \Delta H_x{}^\circ$ at low $[OH^-]$, while at high $[OH^-]$ when the rate is virtually independent of its concentration $\Delta H_{obs.}{}^\ddagger = \Delta H_x{}^\ddagger$ for case (*i*) and $\Delta H_x{}^\ddagger + (\Delta H_x{}^\circ - \Delta H_y{}^\circ)$ for case (*ii*). A similar conclusion, that all relevant $\Delta H_i{}^\circ$ values are close to zero, can be reached in case (*iii*); if any of the contributing $\Delta H_i{}^\circ$ values were significantly different, the Eyring plots would be curved as the relative contributions of the different pathways changed with temperature.

Because it is not possible at this time to assign the individual rate and equilibrium constants in an unambiguous fashion, we are still unable to assign a value to the largest k_2 rate constant for the dissociation of any of the conjugate bases. Nevertheless it is possible to assign lower limits and thereby estimate the minimum enhancement of labilisation that results from deprotonation.

It is possible to make a reasonable assumption about the site of the labilising amido group from the consideration of many other systems. The most effective site is *cis* to the leaving group[9] and a nitrogen that is 'flat', *i.e.* at the centre of a meridional set of three linked donors, is more effective than one that is 'bent', *i.e.* at the centre of a facial set of three linked donors.[10] This makes N(4) the most likely site.

While it is unambiguously shown that the acidity of the picdien and picditn substrates varies considerably with the nature of the acido ligand and the pentadentate ligand, little is known about the factors that determine the acidity of amine protons and there is no firm basis upon which to assign the equilibrium constant to a particular nitrogen atom. This constant, K, can be identified with the ratio, k_1/k_{-1}, and k_1 can be measured for each of the amine protons. Many studies have been made of the way in which the rate constant for proton exchange depends upon the nature of the amine and the other ligands in cobalt(III) complexes[1] and, in general, these rate constants are much more sensitive to variation in the nature of the ligand in the *trans* position.[11] Within the limits of the picdien and picditn complexes studied, the most labile proton for exchange is found on the nitrogen *trans* to the acido group, *i.e.* N(2). It has often been assumed that k_1 can be used as a measure of K, presumably in the mistaken belief that reprotonation is diffusion controlled and k_{-1} therefore essentially constant. For the $[\text{Co(picdien)X}]^{2+}$ cations, the rate constants for the exchange of the proton *trans* to X are approaching diffusion-control values and, where measured,[2] are not very sensitive to the nature of X. The acidity must therefore be controlled in part by the reprotonation rate constant, k_{-1}. It is therefore rash to assume that the most acidic amine group is the one with the most labile proton.

The acidity of the nitro and thiocyanato picdien species is clearly at least two orders of magnitudes greater than that of the other species. It is possible to account for the acidity-enhancing properties of the nitro group in terms of stabilisation of the conjugate base, whereby the π-acceptor nitro group interacts with the π-donor amido group, acting through the t_{2g} orbitals on the cobalt. The ability of NCS to function in the same way is more problematical. The formulation Co–N≡C–S would suggest that it might act as a π acceptor, but Gutterman and Gray[12] have shown that, while the lowest unfilled orbital on the NCS ligand is of π symmetry, it is concentrated on the central carbon atom and the ligand is less able to act as a π acceptor than CN$^-$. The electronic spectrum of $[\text{Co(CN)}_5\text{(NCS)}]^{3-}$ provides no evidence for the participation of π-acceptor orbitals of the triatomic ligand in metal–ligand bonding, but the five cyanide ligands dominate any π-acceptor interaction and the pentacyano complex does not make a valid comparison with the picdien and picditn species. The Co–N–N bond of the azido group is bent (116.7 ± 0.9°[3]) and can be represented as $\text{Co–}\ddot{\text{N}}\text{=N=N}$ in which form it is unable to act as a π acceptor. The ligand-field strengths certainly decrease along the sequence $-\text{NO}_2 > -\text{NCS} > \text{N}_3$.[12]

The difference in the behaviour of the picdien and picditn thiocyanato complexes cannot be explained by any change in the isomeric form. Single-crystal *X*-ray diffraction studies show that both possess the $\alpha\beta$-*anti* configuration with the thiocyanate bound through nitrogen. The increase in the ring size of the ligand decreases the acidity of the most acidic amine proton by a factor of at least 30. The dimensions of the thiocyanate ligands in the two complexes are virtually identical although the Co–N–C bond is more bent in the picdien system, possibly as a result of packing considerations.[3] The strain in the C–N(4)–C bond angle (116°) in all the picdien complexes studied is relieved by the increase in ring size (109° in all the picditn analogues), and it is not impossible that the ring strain is the cause of the enhanced acidity. The answer to this question must await the results of a study of the proton-exchange kinetics of these picditn complexes, currently made difficult by the low solubility of the available complexes in suitable solvents.

The change in reactivity, as expressed by k_{OH}, on going from the picdien to the picditn system requires further consideration. The azido and isothiocyanato complexes show a moderate (two- to four-fold) increase in $k_{\text{OH}}[\Sigma(k_2{}^iK_i)]$ when the chelate ring sizes are increased, which is of a comparable magnitude to that observed for the more labile chloro- and bromo-complexes.[2] The nitro complex, on the other hand, shows a 25-fold increase in reactivity, as well as losing the saturation behaviour on going from the picdien to the picditn system. Whether this is due to the fact that we are studying a different isomeric form (the orange-red colour of the picdien species is not inconsistent with its formulation as a nitrito species) must await the results of a single-crystal *X*-ray diffraction analysis. The system is under investigation.

Conclusion

The limiting rate constants derived from the large deviations from the first-order dependence on $[\text{OH}^-]$ found in the base hydrolysis of the nitro and isothiocyanato picdien cobalt(III) complexes represent the lower limit for the rate constants for the dissociation of the amido conjugate base. As in the case of the chloro- and bromo-complexes,[2] the removal of a suitably situated amine proton increases the lability of the complex by many orders of magnitude. The uncatalysed displacement of Cl$^-$ from *anti*-$\alpha\beta$-$[\text{Co(picdien)Cl}]^{2+}$ is very slow; the rate constant extrapolated from 70 °C is estimated to be about 10^{-7} s^{-1} at 25 °C. Thiocyanate is likely to be much more difficult to displace, for example on changing X from Cl to NCS the rate constant for the uncatalysed aquation of the $[\text{Co(NH}_3)_5\text{X}]^{2+}$ complexes decreases by a factor of 5×10^3,[1] and the nitro complex is much less labile than this. By simply adding orders of magnitude the enhancement of reactivity resulting from the removal of a suitable amine proton from the picdien complexes can be estimated to be a factor that is well in excess of 10^{14}. It is hard to see how the accepted mechanism for labilisation, namely the stabilisation of the five-co-ordinate intermediate by π donation from the amido nitrogen, can account for such a dramatic enhancement.

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