Proton Exchange in the Base Hydrolysis of Deuteriated *trans*-Dichlorobis(ethylenediamine)cobalt(III) and *trans*-Dichloro[(*RS*)-1,9-diamino-3,7-diazanonane]cobalt(III) Cations

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The extent of replacement of the labelled amine protons in the complexes *trans*-$[Co(en)_2Cl_2]^+$ (en = ethylenediamine) and *trans*-$[Co(ddn)Cl_2]^+$ [ddn = (*RS*)-2,3,2-tet = (*RS*)-1,9-diamino-3,7-diazanonane] during base hydrolysis has been measured in the substrate and product as a function of the extent of reaction. The results are consistent with a dissociative conjugate-base mechanism and, in the en complex, the ratio of the rate constants for the reprotonation of the conjugate base (k_{-1}) and its dissociation (k_2) lies within the range $10 > k_{-1} : k_2 > 4$. The active conjugate base from the ddn complex has lost a secondary amine proton and $5 > k_{-1} : k_2 > 0{\cdot}5$. The anomalously fast base hydrolysis of these complexes arises mainly from the unusually high lability of their conjugate bases. Rate constants for base hydrolysis of the *N*-deuteriated complexes are compared with those of the untreated complexes

IN reactions of type (1), the second-order rate constants

$$[Co(en)_2(A)Cl]^{n+} + OH^- \longrightarrow [Co(en)_2(A)OH]^{n+} + Cl^- \quad (1)$$

are, as a rule, not greatly sensitive to the nature or the position of ligand A.[1] The exceptions to this rule are of some interest, *e.g.* when A = *trans*-Cl [2,3] (to a lesser extent *cis*-Cl [2,3]), *trans*-Br,[3] or *cis*-pyridine (or substituted pyridines) [4] the complexes are between 10^2 and 10^3 times more sensitive to base hydrolysis than the other members of the series. As part of a study attempting to understand the causes of these differences, we have started to examine the details of the proton-exchange phenomena that accompany these reactions. A considerable amount of work has been published on the kinetics of proton exchange in metal amine complexes but very little of this has been carried out on systems actually undergoing base hydrolysis. Some years ago we published a preliminary report [5] showing that proton exchange and base hydrolysis of the complex *trans*-$[Co(cyclam)Cl_2]^+$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane) occurred at comparable rates and that each act of base hydrolysis resulted in the exchange of one proton. The i.r. technique used could only provide semiquantitative data so we developed methods using ^1H n.m.r. spectroscopy to provide a quantitative answer which also allow the exchanging protons to be identified when there are non-equivalent sets within the complex.

RESULTS

Kinetics of Base Hydrolysis.—Base hydrolysis of the complex *trans*-$[Co(en)_2Cl_2]^+$ (en = ethylenediamine) has been studied in detail by fast-mixing techniques [2,3] and we have now re-examined these kinetics in buffer solutions at lower pH, using both the untreated and fully *N*-deuteriated samples. It has long been established that the product of the first stage of base hydrolysis is almost entirely *trans*-$[Co(en)_2(OH)Cl]^+$ (ref. 3) and, while this complex is not very sensitive to base hydrolysis (k_B 0·56 l mol^{-1} s^{-1} at 25 °C),[3] it readily undergoes spontaneous aquation (k_A $1{\cdot}6 \times 10^{-3}$ s^{-1} at 25 °C).[6] The overall solvolytic behaviour of the complex *trans*-$[Co(en)_2Cl_2]^+$ therefore depends very much on the pH of the solution. At pH values below 7 (but not too far below since the reactive hydroxo-complex is in acid-base equilibrium with the more inert aquo-complex) the reaction is controlled by the base catalysed loss of the first chloride ligand; the uncatalysed loss of the second chloride is fast in comparison and the process approximates to a single stage in which two chlorides are lost. Between pH 7 and 9 the two steps are of similar rate and at pH > 10 the first step becomes considerably faster than the second.

In the temperature and pH range convenient for spectrophotometric study, the two steps are of comparable rates and overlap and so the kinetics were studied at the wavelength corresponding to the isosbestic point for the second step (*ca.* 570 nm). Rate constants were determined from plots of $\log_{10}(A_\infty - A_t)$ against time, where A_t and A_∞ are the optical densities at time *t* and the isosbestic point respectively. The base hydrolysis of the $[NNN'N'\text{-}^2H_4]$ complex was followed in a similar way but plots of $\log_{10}(A_\infty - A_t)$ against time were non-linear, the gradient increasing as the reaction proceeded. This is due to a parallel proton exchange reaction (see below) which generates the more reactive proto complex. Rate constants were determined from the initial gradients and are collected in Table 1.

Base hydrolysis of the complex *trans*-$[Co(ddn)Cl_2]^+$ [ddn = (*RS*)-2,3,2-tet = (*RS*)-1,9-diamino-3,7-diazanonane] has been studied in detail by Niththyananthan [7] in buffer solution and by Tucker using stopped-flow techniques [8] and the full details will be published elsewhere. The rate constant is some 20 times larger than that for the corresponding bis(en) complex, and the spontaneous aquation of *trans*-$[Co(ddn)(OH)Cl]^+$, the first product of base hydrolysis (k_A 3×10^{-2} s^{-1} at 13 °C),[8] is *ca.* 100 times faster. The study of the base hydrolysis of the $[NNN'N''N'''N'''\text{-}^2H_6]$ complex and the untreated complex was carried out spectrophotometrically in the pH range 5—6. Under these

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[1] M. L. Tobe, *Accounts Chem. Res.*, 1970, **3**, 377.

[2] R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Amer. Chem. Soc.*, 1956, **78**, 709.

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[4] F. Basolo, J. G. Bergmann, R. E. Meeker, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1956, **78**, 2676; S. C. Chan and C. L. Lee, *J. Chem. Soc. (A)*, 1969, 2649.

[5] C. K. Poon and M. L. Tobe, *Chem. Comm.*, 1968, 156.

[6] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 1961, 4637.

[7] R. Niththyananthan, Ph.D. Thesis, University of London, 1970.

[8] M. L. Tobe and M. L. Tucker, *Inorg. Chem.*, in the press.

conditions, spontaneous aquation of the *trans*-chlorohydroxo-product is fast and only one stage of reaction was observed. The rate constants (Table 1) were determined in *the usual* way from absorbance data at 530 nm where there is the maximum change in optical density. In this system the deuteriated complex gave linear semilogarithmic plots over more than 1 half-life, indicating the lack of significant exchange at the nitrogen atom involved.

TABLE 1

Rate constants for base hydrolysis of untreated and *N*-deuteriated *trans*-dichlorobis(ethylenediamine)cobalt(III) cations and *trans*-dichloro[(*RS*)-1,9-diamino-3,7-diazanonane]cobalt(III) cations in basic aqueous solution

Temp. (t/°C)	pH	10^6[OH⁻] / M	10^4k_{obs} / s^{-1}	k_B / l mol^{-1} s^{-1}
trans-$[Co(en)_2Cl_2]^+$ [Complex] = 3 × 10^{-3}M, [Buffer] = 10^{-1}M				
(*a*) Untreated				
13·8	8·52	1·34	8·1	610
17·2	8·42	1·42	15·5	1 090
21·0	8·31	1·52	24·3	1 600
25·6	8·17	1·58	43	2 700
30·0	8·09	1·54	76	4 900
30·5	7·92	1·27	63	4 900
(*b*) [*NNN′N′*-$^2H_4$]				
13·5	8·53	1·31	3·8	290
17·4	8·42	1·42	8·6	590
21·0	8·31	1·52	12·5	820
25·6	8·17	1·58	25·7	1 630
30·5	7·92	1·27	46	3 600
trans-$[Co(ddn)Cl_2]^+$ [Buffer] = 5·0 × 10^{-2}M				
(*a*) Untreated				
25·0	6·09	0·0040	7·9	64 000
25·0	6·09	0·011	7·7	62 000 [b]
(*b*) [*NNN′N″N‴N‴*-$^2H_6$]				
25·0	6·09	0·0025	4·0	32 000 [a]
25·0	6·09	0·011	4·25	35 000 [b]

ddn = (*RS*)-1,9-Diamino-3,7-diazanonane.

[a] [Complex] = 2·5 × 10^{-3}M, I = 1·7 × 10^{-2}M. [b] [Complex] = 5·0 × 10^{-3}M, I = 3·0 × 10^{-2}M.

Proton-exchange Studies.—trans-$[Co(en)_2Cl_2]^+$. In order to relate proton exchange to the base hydrolysis it was necessary to examine the unreacted and the reacted materials separately. Use was made of the fact that the complex *trans*-$[Co(en)_2Cl_2]ClO_4$ is virtually insoluble in 10^{-1}M-perchloric acid and that the reaction products can be converted back to this in acid solution under conditions where no significant proton exchange occurs. Using *trans*-dichlorobis{[*NNN′N′*-$^2H_4$]ethylenediamine}-cobalt(III) chloride in aqueous solution at 0 °C and pH 10·0 (maintained by pH-stat), the progress of the reaction was controlled by the amount of alkali consumed and by the weight of *trans*-$[Co(en)_2Cl_2]ClO_4$ recovered as unreacted material. The very close agreement between the two figures (Table 2) indicates that the replacement of the second chloride ligand does not contribute significantly to the consumption of hydroxide ion until the later stages of the reaction. The extent of proton transfer was determined by dissolving a fixed amount of complex in dimethyl sulphoxide containing benzene as an internal standard and measuring the ^1H n.m.r. spectrum. The amine protons absorbed as a broadish peak 2·14 p.p.m. upfield from the sharp resonance of the benzene protons. Since, in dimethyl sulphoxide these appear at τ 2·63 [τ 10(Me_4Si)], the amine protons absorb at τ 4·77. The integrated areas under the peaks were standardised by comparison with the benzene peak and the value corresponding to 8 protons per complex was determined by using an untreated sample of *trans*-$[Co(en)_2Cl_2]ClO_4$. The data are reported in Table 2.

The proton-exchange properties of the reaction product, *trans*-$[Co(en)_2(OH)Cl]^+$, were examined separately. The complex was dissolved in D_2O at 0 °C and, after 10 min, the solution was acidified with hydrochloric and perchloric acids and the complex converted, on warming, to the insoluble *trans*-$[Co(en)_2Cl_2]ClO_4$. The ^1H n.m.r. spectrum showed that there was no significant exchange and this was confirmed by the i.r. spectrum. When the reaction was carried out in borate buffer at 0 °C in D_2O, 'pH' 10, the complex recovered after 10 min had exchanged only *ca.* 0·4 of a proton. The same results could be obtained by the pH-stat method, provided the same sodium hydroxide solution (NaOD in D_2O) used to bring the pH to 10 was sufficiently dilute (*ca* 10^{-3}M). With stronger alkali extensive exchange occurred.

trans-$[Co(ddn)Cl_2]^+$. Base hydrolysis is too fast for the pH-stat method to be applied, even at 0 °C, and the original method using buffer solutions was adopted. Preliminary experiments showed that the buffer aminium perchlorate was either not precipitated with the complex or else could be readily washed away with dilute perchloric acid. *trans*-Dichloro{[*NNN′N″N‴N‴*-$^2H_6$](*RS*)-1,9-diamino-3,7-diazanonane}cobalt(III) chloride was dissolved in 2,6-dimethylpyridine–nitric acid buffer at 25·0 °C, pH 6·19, and aliquot portions were withdrawn at appropriate times and poured into an excess of dilute perchloric acid. The unreacted perchlorate salt was precipitated and could be separated from the soluble product, which could then also be converted to the perchlorate salt of the dichloro-complex. The extent of reaction was followed by weighing the recovered unreacted material and by parallel spectrophotometric studies. The extent and position of proton exchange was followed by the method described above. The untreated complex in dimethyl sulphoxide showed two peaks that can be assigned to the N–H protons with areas in the ratio 1 : 2 at 1·20 and 1·97 p.p.m. upfield from benzene, corresponding to τ 3·83 and 4·60. These are assigned to the secondary and primary amine protons respectively. The relative exchange was measured as before and the results are collected in Table 3.

An experiment was carried out in which the isotopic labelling was reversed.* A solution of 2,6-dimethylpyridine–HNO_3 buffer was prepared in D_2O and the untreated complex used. The reaction was quenched by adding dilute perchloric acid when the colour indicated *ca.* 50% reaction. The unreacted perchlorate salt was treated in the usual way. The i.r. spectrum contained peaks at 2 386 and 2 460 cm^{-1} assignable to N–D stretching modes and the n.m.r. showed that exchange had taken place mainly at the secondary nitrogen atoms. A comparison with the standard indicated that 0·65 secondary amine and 0·4 primary amine protons were exchanged.

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TABLE 2

Exchange of protons in the base hydrolysis of the *trans*-dichlorobis{[*NNN'N'*-$^2H_4$]ethylenediamine}cobalt(III) cation at 0·0 °C and pH 10·0. [Complex] = 5·00 × 10^{-2}M

Moles of base consumed per mole of complex	Weight of material recovered [a] mg		Moles of unreacted perchlorate recovered per mole of complex used	Relative exchange [b]		Number of N–H protons exchanged	
	Unreacted	Reacted		Unreacted	Reacted	Unreacted	Reacted
0·15	218	34	0·81	0·036	0·070	1·17	2·22
0·29	190	49	0·71	0·058	0·077	1·84	2·45
0·30	177	49	0·66	0·055	0·083	1·74	2·67
0·40	166	51	0·62	0·066	0·089	2·10	2·83
0·50	134	57	0·50	0·087	0·100	2·77	3·16
0·75	67	139	0·25	0·123	0·135	3·91	4·28
0·91	37	178	0·17	0·132	0·148	4·18	4·70

[a] The sum of the weights of reacted and unreacted perchlorates should be constant (271 mg). The major loss is incurred in the recovery of the reacted material. [b] Relative exchange = (area under N–H peak at τ 4·77)/(area under reference peak at τ 2·63); relative exchange for fully protonated sample = 0·315 ≡ 8 protons.

TABLE 3

Exchange of deuterium in the base hydrolysis of the *trans*-dichloro{[*NNN'N''N'''N'''*-$^2H_6$](*RS*)-1,9-diamino-3,7-diazanonane}cobalt(III) cation in aqueous solution at pH 6·19 [a] and 24·5 °C

t/s	Weight of unreacted material (mg/10 cm^3 sample)	Weight of product recovered (mg/10 cm^3 sample)	Moles of unreacted perchlorate per mole of complex used	No. of deuterons exchanged Unreacted		Reacted	
				>ND	–ND_2	>ND	–ND_2
120	106	10	0·89	0·0	0·0	1·2	0·7
360	90	21	0·76	0·0	0·0	1·6	1·1
720	78	33	0·65	0·0	0·0	2·0	1·9
1 200	66	36	0·56	0·0	0·0	2·0	1·9
1 825	54	54	0·46	0·1	0·4	2·0	2·5
2 [b]	0·0	*c*	0·0			2·0	4·1
2 [d]	0·0	*c*	0·0			1·5	1·3
2 [e]	0·0	*c*	0·0			1·8	0·7

[a] 2,6-Dimethylpyridine–HNO_3 buffer (3 × 10^{-1}M), [Complex] = 3·0 × 10^{-2}M. [b] 2·5 × 10^{-1}M-NaOH, 2·5 × 10^{-3}M-complex. [c] Not measured. [d] 2·5 × 10^{-2}M-NaOH, 2·5 × 10^{-3}M-complex. [e] 5·0 × 10^{-3}M-NaOH, 2·5 × 10^{-3}M-complex.

DISCUSSION

The dissociative conjugate-base mechanism for the base-catalysed solvolysis of certain cobalt(III) ammine and amine complexes, as first proposed by Garrick,[9] involves the sequence of reactions (2)—(5) which leads

$$[CoL_4(NHR_2)X]^{n+} + OH^- \xrightarrow{k_1} [CoL_4(NR_2)X]^{(n-1)+} + H_2O \quad (2)$$

$$[CoL_4(NR_2)X]^{(n-1)+} + H_2O \xrightarrow{k_{-1}} [CoL_4(NHR_2)X]^{n+} + OH^- \quad (3)$$

$$[CoL_4(NR_2)X]^{(n-1)+} \xrightarrow{k_2} [CoL_4(NR_2)]^{n+} + X^- \quad (4)$$

$$[CoL_4(NR_2)]^{n+} + H_2O \xrightarrow{\text{fast}} [CoL_4(NHR_2)X]^{n+} \quad (5)$$

to a rate law of the form (6), provided that the concentration of the amido-conjugate base is always small.

$$-d[CoL_4(NHR_2)X]/dt = k_1k_2[CoL_4(NHR_2)X][OH^-]/(k_{-1} + k_2) \quad (6)$$

(L = unidentate ligand, R = a substituent which may be H, X = unidentate leaving group.) In the cases first considered, *e.g.* $[Co(NH_3)_5X]^{2+}$, $k_{-1} \gg k_2$ and steps (2) and (3) constituted a fast-pre-equilibrium protolytic process and the rate expression reduces to (7) (where $K = k_1/k_{-1}$). This might also allow the situation

$$-d[CoL_4(NHR_2)X]/dt = Kk_2[CoL_4(NHR_2)X][OH] \quad (7)$$

where the concentration of conjugate base is not necessarily negligible and then the dependence on $[OH^-]$ would be modified as in equation (8).

$$-d[CoL(NHR_2)X]/dt = Kk_2[CoL_4(NHR_2)X][OH^-]/(1 + K[OH^-]) \quad (8)$$

The labelling experiments with the [*NNN'N'*-$^2H_4$]en and [*NNN'N''N'''N'''*-$^2H_6$]ddn complexes indicate unambiguously that the proton-transfer processes are not fast compared to the rate of base hydrolysis. The ddn complex presents the closest approach to the other limit, *i.e.* that in which the removal of the proton becomes the rate-determining step. A study of the isotopic distribution in the recovered unreacted material indicates no loss of deuterium until about 1 half-life when some exchange is observed at the primary nitrogen atom which, as we shall see below, is not the site at which the active conjugate base is deprotonated. At first sight this might suggest that every act of dedeuteriation leads to base hydrolysis and that the conjugate base, when formed, dissociates before it can be reprotonated, but this is not necessarily so. The

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[9] F. J. Garrick, *Nature*, 1937, **139**, 507.

very marked isotope effect suggests that, if the conjugate base did take up a proton, the $[^2H_5]$complex would be expected to lose this proton in a subsequent attack by base *ca.* 2 times more readily than its other secondary amine deuterons, so that a small amount of reprotonation would not be detected. By examining the behaviour of the $[^2H_5]$complex in D_2O buffers, the deuteriation of the conjugate base is 'frozen' because now the remaining proton is twice as likely to be lost than the returned deuteron. The observation that up to 0·65 of the proton is replaced by deuterium in the unreacted material recovered after 1 half-life indicates that k_{-1} is not negligible compared to k_2.

The reaction product of base hydrolysis of the complex *trans*-$[Co(ddn)Cl_2]^+$ at pH 6·19 appears to have undergone complete exchange at the secondary nitrogen atoms except possibly at the earliest stages of the reaction. The extent to which the low values are due to incomplete separation of the unreacted dichloro-complex is clear but, when there is only a small amount of reaction product to recover, contamination by a small amount of unrecovered substrate has its maximum effect. The low exchange of the primary amine protons is real and cannot be explained in this way. While these results do not prove beyond doubt that a proton (deuteron) is exchanged in each act of base hydrolysis (a fundamental requirement of the S_N1cb mechanism), they do indicate that *if deprotonation has taken place it must have occurred at one of the secondary nitrogen atoms.*

The observation that the exchange of the deuterons in the unreacted material take place mainly on the primary amine nitrogen atoms suggests that the conjugate base with the lone pair on the primary nitrogen atom is considerably less susceptible to dissociative loss of chloride ligand than that with the lone pair on the secondary nitrogen. In these reactions carried out at pH 6·19, conversion of the *trans*-chlorohydroxo-product to the *trans*-dihydroxo-species is fast compared to the first step and the material recovered has been in the form of *trans*-$[Co(ddn)(OH)_2]^+$ for a significant time before protonation and anation and it is probable that exchange of the primary amine deuterons (and possibly the secondary amine ones as well) takes place while the complex is in this form. For a process of type (9)

$$\begin{tikzcd} trans\text{-}[Co\{(^2H_6)ddn\}Cl_2] \arrow[r, "k_B"] & trans\text{-}[Co\{(^2H_4)ddn\}(OH)Cl]^+ \arrow[d, "\text{fast}"] \\ trans\text{-}[Co(ddn)(OH)_2]^+ & trans\text{-}[Co\{(^2H_4)ddn\}(OH)_2]^+ \arrow[l, "k_D"'] \end{tikzcd} \qquad (9)$$

it can easily be shown * that equation (10) is applicable,

$$N_{exch} = 4\{[1 - (k_D - k_B)^{-1}][k_D\exp(-k_Bt) - k_B\exp(-k_Dt)]\}[1 - \exp(-k_Bt)]^{-1} \qquad (10)$$

where N_{exch} is the average number of primary amine protons per molecule of recovered product and k_B and k_D are pseudo-first-order rate constants for base hydrolysis of the dichloro-complex and proton exchange of the dihydroxo-product respectively, at the pH and temperature used. The data in Table 3 best fit the calculated curve when k_D *ca.* $1·2 \pm 0·2 \times 10^{-3}$ s^{-1}. It is not yet possible to say whether or not this rate constant is dependent on pH but work is in hand to examine this aspect of the problem in much greater detail.

The set of experiments carried out in the presence of an excess of alkali were designed to examine the composition and properties of the *trans*-chlorohydroxo-intermediate. At pH > 10·5 and 25 °C it has been confirmed by independent spectrophotometric and titrimetric techniques that the loss of the first chloride ligand is complete before there is any significant hydrolysis of the chlorohydroxo-product.[8] In the experiments with $2·5 \times 10^{-3}$ $(5·0 \times 10^{-3})$, $2·25 \times 10^{-2}$ $(2·5 \times 10^{-2})$, and $2·5 \times 10^{-1}$M-NaOH at 0 °C (figures in parentheses indicate the initial concentration of hydroxide ion), the acidified product was almost entirely *trans*-$[Co(ddn)(H_2O)Cl]^{2+}$ but the extent of deuterium exchange varied considerably. Since the time between adding the base and the acid was fairly constant (1—2 s, the longer time being for the lowest hydroxide-ion concentration), it must be assumed that the exchange of the primary amine deuterons in the complex *trans*-$[Co(ddn)(OH)Cl]^+$ is base catalysed (at least in part) and that the rate of exchange of these protons (an order of magnitude estimate gives $k = 10$ l mol^{-1} s^{-1} at 0 °C) is considerably faster than the base hydrolysis. A direct study of these exchange kinetics is in hand. The exchange of the secondary amine protons appears to be virtually complete in most of the samples examined and so it is still not possible to distinguish between exchange at the secondary amine arising from base hydrolysis and that due to a subsequent process in the reaction product.

The analogous studies with the $[NNN'N\text{-}^2H_4]$en dichloro-complex indicate less extreme behaviour. Sampling experiments were conveniently carried out at a pH where the chlorohydroxo-complex does not undergo significant solvolysis or proton exchange during the time needed for base hydrolysis of the dichloro-complex. The recovered unreacted material showed significant proton exchange but in all cases the exchange was less than that found in the recovered product. Plots of the amount of exchange, in the reacted and unreacted material, as a function of total reaction when extrapolated to zero reaction had intercepts that differed by at least one proton {part of this, in the recovered product, arises from subsequent exchange in the complex *trans*-$[Co(en)_2(OH)Cl]^+$} (Figure). We attempted to calculate expressions for the quantities plotted in this Figure but were unable to solve the equations when kinetic-isotope effects were taken into account in the deprotonation (k_1) step. If it is assumed that there is no isotope effect (an obviously false assumption

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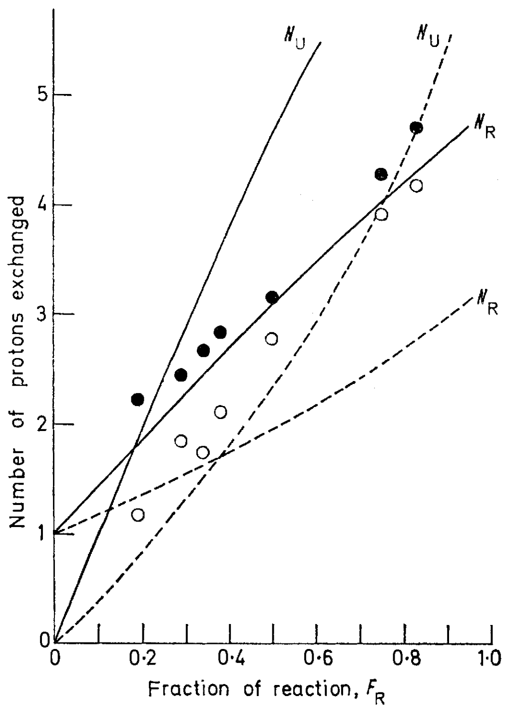
* The derivation of equation (10) is to be found in Supplementary Publication No. SUP 20748 (8 pp., 1 microfiche). For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (*items* less than 10 pp. are supplied as full size copies).

in the light of the experimental evidence), expressions can be derived which fit the data reasonably well if it is assumed that $k_{-1} \sim 4k_2$. However, since it would be easier to remove a proton than a deuteron, the amount of exchange observed in both the reacted and the unreacted material would be less than that calculated assuming no isotope effect and the departure would become more pronounced as the reaction proceeded. The factor of 4 therefore represents a lower limit to the ratio of k_{-1} to k_2 but the relation between the fraction exchanged and the fraction of reaction is so sensitive to $k_{-1} : k_2$ that an upper limit of 10 to this ratio is probably an overestimate.



Extent of amine proton exchange in the unreacted complex *trans*-$[Co(en)_2Cl_2]^+$ (○) and in the recovered product (●) plotted as a function of the extent of reaction, F_R. The lines are calculated from the theoretical expressions (see SUP No. 20748) $N_U = 8[1 - (1 - F_R)^{(k_{-1}/8k_2)}]$ and $N_R = 8\left[1 - \frac{7k_2}{k_{-1} + 8k_2}\left\{\frac{1 - (1 - F_R)^{(1 + k_{-1}/8k_2)}}{F_R}\right\}\right]$, where N_U and N_R are the average number of amine protons per molecule of unreacted and reacted complex, respectively, when the fraction of reaction is F_R, and represent the cases where $k_{-1} = 4k_2$ (– – – –) and $k_{-1} = 10k_2$ (——). No correction has been made for the subsequent exchange in the complex *trans*-$[Co(en)_2(OH)Cl]^+$, which will lead to an increase in the experimental values of N_R and become more serious as F_R increases (*ca.* 0·4 protons when $F_R = 0·5$). The calculated expressions ignore the known isotope effects that will favour the removal of H with respect to D. This will cause the experimental values for N_U to become smaller than predicted by the above expression as the reaction proceeds and will similarly affect the values of N_R, but to a lesser extent

It is now possible to examine the problem of the unusually high reactivity of the *trans*-tetra-aminedichloro-series of complexes. Since the observed second-order rate constant for base hydrolysis $k_B = nk_1k_2/(k_{-1} + k_2)$ [see equation (5)], where n is the number of equivalent protons that can be removed, some limits can be set to the value of k_1, the rate constant for deprotonation, if a reasonable estimate can be made of values of the ratio $k_{-1} : k_2$ [k_1 would be the rate constant obtained from the plot of $(F_\infty - F_t)$ against time (where F_t and F_∞ are fractions of exchange of the amine protons at time t and at the end of the reaction, F_∞ generally being unity) if there were no complications from base hydrolysis]. For the complex *trans*-$[Co(en)_2Cl_2]^+$ this ratio is definitely >4 and probably <10 and so $1·9 \times 10^3 < k_1 < 4·0 \times 10^3$ l mol^{-1} s^{-1} at 25 °C; for *trans*-$[Co(ddn)Cl_2]^+$, the ratio must lie between 0·5 and 5, so that $4·8 \times 10^4 < k_1 < 1·9 \times 10^5$ l mol s^{-1} at 25 °C, $I = 1·7 \times 10^{-2}$M. Published rate constants for proton exchange in complexes of this type, where base hydrolysis does not interfere, indicate clearly that the rate of deprotonation is markedly dependent on such features as the charge of the complex, the nature and position of the ligands present, and the nature, stereochemistry, and environment of the amine proton concerned. The values obtained for the complex *trans*-$[Co(en)_2Cl_2]^+$ lie within the range expected for *trans*-dianiono-complexes bearing a single positive charge, for example for *trans*-$[Co(en)_2X_2]^+$ complexes $k_{exch} = 6·8 \times 10^4$ for $X = NO_2$ [10] and $1·0 \times 10^3$ l mol^{-1} s^{-1} for $X = F$ [10] at 25 °C.

The major part of the enhanced reactivity to base hydrolysis must either arise from an anomalously high rate of dissociation of the conjugate base (k_2) or an anomalously low rate of reprotonation of the conjugate base (k_{-1}). The proton-labelling experiments show clearly that the ratio $k_2 : k_{-1}$ is markedly increased in these dichloro-complexes when compared to $[Co(NH_3)_5Cl]^{2+}$, for example, but they do not allow us to pin-point the cause. In principle, it may be possible to increase the concentration of the base to the point where $k_1[OH^-] \gg k_2$. Under these circumstances it would no longer be possible to assume steady-state conditions for the concentration of the conjugate base and a limiting rate, independent of the concentration of hydroxide ion, would be approached. A major part of the substrate would be in the form of the conjugate base and the limiting first-order rate constant would be k_2. There is no evidence for any departure from the first-order dependance of rate on hydroxide-ion concentration up to 10^{-1}M-OH$^-$ for the reaction with the complex *trans*-$[Co(ddn)Cl_2]^+$, nor is there any evidence for the build-up of significant concentrations of the conjugate base, so that k_2 must therefore be greater than 10 times the highest pseudo-first-order rate constant observed, *i.e.* $>1·2 \times 10^3$ s^{-1}.[8] The reason why the conjugate base is so labile is not immediately obvious. The conjugative assistance by the lone-pair on the amido-ligand has been thought by many to be the major labilising factor and there is no strong evidence to cause one to doubt this. Why this should be enhanced by halogen (F, Cl, or Br) and not affected by OH (usually a stronger labiliser than the halogens) is still not clear.

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[10] J. W. Palmer and F. Basolo, *J. Phys. Chem.*, 1960, **64**, 778.

EXPERIMENTAL

trans-*Dichlorobis(ethylenediamine)cobalt*(III) *Chloride*.—This complex was prepared by the method of Bailar and Rollinson [11] and purified by recrystallisation from water (Found: C, 16·8; H, 5·7; Cl, 37·1; N, 19·6. Calc. for $C_4H_{16}Cl_3CoN_4$: C, 16·9; H, 5·6; Cl, 37·2; N, 19·6%).

trans-*Dichlorobis*([NNN'N'-$^2H_4$]*ethylenediamine*)*cobalt*(III) *Chloride*.—Untreated *trans*-$[Co(en)_2Cl_2]Cl$ (en = ethylenediamine) was dissolved in D_2O and the solution made alkaline by the addition of LiOH and set aside overnight. An excess of hydrochloric acid was added and the solution heated to dryness on a water-bath. The resulting green crystals of the hydrochloride adduct were heated at 110 °C. This process was repeated four times and the final crude product was recrystallised rapidly from warm water (35 °C). The i.r. spectrum showed only traces of peaks assigned to N–H stretching and bending modes and corresponded closely with that reported in the literature (Found: Cl, 36·5. Calc. for $C_4H_8Cl_3CoD_8N_4$: Cl, 36·3%).

The complex *trans*-chlorobis(ethylenediamine)hydroxocobalt(III) chloride was kindly supplied by Miss M. Tucker.

trans-*Dichloro*[(RS)-1,9-*diamino*-3,7-*diazanonane*]*cobalt*(III) *Chloride*.—This complex was prepared by the method of Bosnich *et al.*[12] (Found: C, 26·2; H, 6·4; N, 17·3. Calc. for $C_7H_{20}Cl_3CoN_4$: C, 25·9; H, 6·2; N, 17·2%).

trans-*Dichloro*([NNN'N''N'''N'''-$^2H_6$](RS)-1,9-*diamino*-3,7-*diazanonane*)*cobalt*(III) *Chloride*.—The complex *trans*-$[Co(ddn)Cl_2]Cl$ [ddn = (*RS*)-1,9-diamino-3,7-diazanonane] (4·4 g) was dissolved in D_2O (10 cm^3), the solution made alkaline (1M) by addition of solid lithium hydroxide, and the resulting solution kept at 60 °C for 2 h. Concentrated hydrochloric acid (10 cm^3) was added and the greenish solution evaporated on a steam-bath until a crust of crystals formed on the surface. The bright green crystals which separated from the cooled solution were filtered off and heated at 110 °C for 5 h (yield 3·6 g). This process was repeated three times in order to obtain a sample that had no ^1H n.m.r. absorption (in DMSO) at τ 3·83 and 4·60 corresponding to the secondary and primary amine protons respectively. In the i.r. spectrum, the five peaks associated with N–H and NH_2 stretching modes, which are observed at 3 255s, 3 192s, 3 135mw, 3 110m, and 3 065m cm^{-1} in the normal complex, were replaced by N–D vibrations at 2 450m, 2 430s, 2 380s, 2 310s, and 2 280m cm^{-1} (Found: C, 25·1; N, 16·8. Calc. for $C_7H_{14}Cl_4CoD_6N_4$: C, 25·3; N, 16·9%).

Kinetics.—Rates of base hydrolysis were studied spectrophotometrically in silica cells in the temperature-controlled cell compartment of a Unicam SP 800 spectrophotometer. In the reaction of the complex *trans*-$[Co(en)_2Cl_2]^+$, in the pH range 8—8·5, the isosbestic point for the loss of the second chloride ligand, which is slightly pH dependent, was located by a preliminary experiment in which the spectrum was scanned repetitively over a narrow range of wavelength (540—600 nm). The spectrophotometer was then locked at the wavelength of the isosbestic point and the reaction repeated under identical conditions, the absorbance change being recorded as a function of time. The temperature, which was measured by a thermometer immersed in the reaction vessel at the end of the reaction, was held constant to better than $\pm$0·1 °C. The pH of the reaction mixture was determined with a Radiometer PHM26 pH-meter using an identical solution at the same temperature. Even though the concentration of buffer was at least 10 times that of the complex, the pH was often observed to change significantly in the course of the reaction. When this was observed the necessary corrections were made. Attempts to use a pH-stat technique to follow the kinetics of base hydrolysis were only partly successful because of the large second-order rate constants for base hydrolysis.

Isotopic-exchange Studies.—A solution of the complex *trans*-$[Co\{(^2H_4)en\}_2Cl_2]Cl$ (0·220 g) in water (15 cm^3) was cooled to 0 °C and the electrode and burette system inserted. Using the combination of Radiometer PHM26, TTT11, ABU11, TTA3, and SBR2 automatic-titration assembly, in pH-stat mode (pH 10·00 $\pm$ 0·03), the reaction was started. When the appropriate amount of base (0·5M-NaOH titrant) had been consumed, the reaction was quenched by adding concentrated perchloric acid. The insoluble complex *trans*-$[Co(en)_2Cl_2]ClO_4$ was precipitated and the mixture was set aside for 10 min in ice. The precipitate was filtered off (the filtrate being retained), washed with 0·1M-perchloric acid, then alcohol and ether, and dried. This separation was carried out under standard quantitative conditions. The filtrate, containing aquochloro- and diaquo-species, was treated with concentrated hydrochloric acid and warmed on a water-bath for 2—3 h. This converted the various species back to the complex *trans*-$[Co(en)_2Cl_2]ClO_4$, which crystallised out on cooling. The mother liquor was almost colourless. This perchlorate salt was separated and treated as before. The extent of proton exchange was determined by dissolving a weighed amount (0·0225 g) of perchlorate salt in dimethyl sulphoxide (0·50 cm^3) containing benzene as internal standard (54·8882 g DMSO + 2·6303 g benzene). The ^1H n.m.r. spectrum was measured on a Varian HA100 instrument and the area under the amine proton peaks measured by integration or by square counting. The process was repeated for different amounts of reaction.

The method could not be applied to the more labile *trans*-$[Co\{(^2H_6)ddn\}Cl_2]^+$ complex and an alternative procedure was adopted. The appropriate amount of complex was dissolved in water previously brought to the reaction temperature (24·5 $\pm$ 0·1 °C). The reaction was started by adding the appropriate amount of 2,6-dimethylpyridine–HNO_3 buffer and the volume adjusted by more water until the concentration of complex was $3·0 \times 10^{-2}$M and that of buffer 0·30M. Aliquot portions were withdrawn from time to time and poured into an excess of perchloric acid (10^2 moles per mole of complex). These aliquot portions were set aside in ice (2 h) to ensure complete precipitation of the perchlorate salt of the dichloro-complex and then allowed to warm to room temperature before filtration. This ensured that there was little or no coprecipitation of 2,6-dimethylpyridinium perchlorate. The rest of the separation and analysis procedure was similar to that for the en complex except that now two amine proton peaks were observed.

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