Base Hydrolysis of Amino-acid Esters and Amides in the Co-ordination Sphere of Cobalt(III). Part II.[1] Hydrolysis of 2-Aminoethyl Acetate

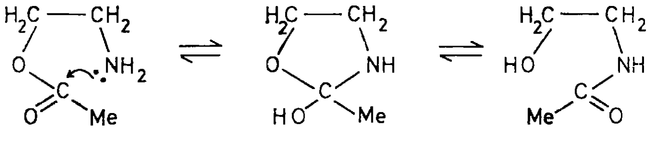
By **Kevin B. Nolan, Brian R. Coles,** and **Robert W. Hay,*** Chemistry Department, University of Stirling, Scotland

Base hydrolysis of the complex *cis*-$[Co(en)_2X(NH_2CH_2CH_2OCOMe)]^{2+}$ (en = ethylenediamine; X = Cl or Br) has been studied by pH-stat and spectrophotometry at 25 °C and $I = 0{\cdot}1$M. Two consecutive reactions occur in basic media. Following loss of halide ion ($k_{OH}{}^{Cl} = 1{\cdot}38 \times 10^3$, $k_{OH}{}^{Br} = 8{\cdot}7 \times 10^3$ l mol^{-1} min^{-1}), slower base hydrolysis of the ester function occurs ($k_{OH}{}^{ester} = 1{\cdot}44 \times 10^2$ l mol^{-1} min^{-1}). Initial base hydrolysis of halide ion is consistent with the observations that (*a*) rate constants for the slow hydrolysis steps in the bromo- and chloro-complexes are identical, within experimental error, and (*b*) a single rate process is observed spectrophotometrically with $k_{OH} = 1{\cdot}42 \times 10^2$ l mol^{-1} min^{-1}. In the pH-stat measurements 2 mol of base are consumed per mol of complex and the final product of the reaction is the penta-aminohydroxo-complex which has been identified by visible spectra and potentiometric titration. The $pK_a{}^P$ value for ionisation (i) is 6·1 at 25 °C and $I = 0{\cdot}1$M.

$$[Co(en)_2OH_2(NH_2CH_2CH_2OH)]^{3+} \rightleftharpoons [Co(en)_2OH(NH_2CH_2CH_2OH)]^{2+} + H^+ \qquad \text{(i)}$$

Hydrolysis of the complex *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OCOMe)]^{2+}$ in *ca.* 6M-hydrochloric acid gives the corresponding penta-aminechloro-complex of 2-aminoethanol. Base hydrolysis of the penta-aminechloro-complex containing *N*-co-ordinated 2-aminoethanol requires 1 mol of base for complete hydrolysis ($k_{OH} = 1{\cdot}23 \times 10^3$ l mol^{-1} min^{-1} by pH-stat and spectrophotometry at 25 °C and $I = 0{\cdot}1$M). It is estimated that base hydrolysis of 2-aminoethyl acetate in the dipositive cobalt(III) complex is some 18 times faster than that for the free ligand and some 2 times faster than that for the protonated ligand. Mercury(II)-catalysed aquations of the complex *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OCOMe)]^{2+}$ and the corresponding 2-aminoethanol derivative have also been studied. The reactions follow a rate law, rate = $k[Hg^{II}][Complex]$ in 0·57M-$HClO_4$. There is evidence for neighbouring-group participation (NGP–5OH) in aquation of the 2-aminoethanol derivative.

THERE has recently been considerable interest[2] in hydrolysis of glycine esters in complexes *cis*-$[Co(en)_2X(NH_2CH_2CO_2R)]^{2+}$ (R = Me, Et, or Pr^i; X = Cl or Br). Hg^{II}- and HOCl-induced removal of bromide ion from the complex $[Co(en)_2Br(NH_2CH_2CO_2R)]^{2+}$ has been shown[3] to proceed *via* the chelated ester intermediate $[Co(en)_2(glyOR)]^{3+}$, previously suggested by Alexander and Busch.[4] Recent papers have also dealt with hydrolysis of amino-acid amides[5] and aminonitriles[6,7] in the co-ordination sphere of cobalt(III), however, nothing has as yet been published on the hydrolysis of esters derived from aminoalcohols. 2-Aminoethyl acetate is a convenient substrate for an investigation of this type.



(I) (II) (III)

Hydrolysis of 2-aminoethyl acetate has been the subject of a number of publications,[8-10] notably those by Hansen[8] and, recently, Schmir.[10] In basic solution 2-aminoethyl acetate (I) undergoes rapid base-catalysed isomerisation to 2-acetylaminoethanol (III) *via* the tetrahedral intermediate (II). Hansen[8] has estimated that k_1 is *ca.* 180—300 l mol^{-1} min^{-1} at 25 °C and $I = 0{\cdot}07$M ($KClO_4$) while k_2 is *ca.* 6—9 l mol^{-1} min^{-1} for reactions (1) and (2).

EXPERIMENTAL

trans-Dichlorobis(ethylenediamine)cobalt(III) chloride was prepared as described by Krishnamurthy,[11] and the bromo-derivative as described by Werner.[12] 2-Aminoethyl acetate hydrochloride was prepared by the method of Crane and Rydon.[13] The product was twice recrystallised

$$\begin{tikzcd}
H_3N^+CH_2CH_2OCOMe + OH^- \arrow[r, "k_1"] \arrow[d, shift left, "pK_a\ 8{\cdot}94"] & H_3N^+CH_2CH_2OH + MeCO_2^- \arrow[d, shift left, "pK_a\ 9{\cdot}60"] & (1) \\
H_2NCH_2CH_2OCOMe + OH^- \arrow[r, "k_2"] \arrow[u, shift left] & H_2NCH_2CH_2OH + MeCO_2^- \arrow[u, shift left] & (2)
\end{tikzcd}$$

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[1] Part I, R. W. Hay, R. Bennett, and D. J. Barnes, *J.C.S. Dalton*, 1972, 1524.

[2] R. W. Hay and P. J. Morris, Metal Ion Promoted Hydrolysis of Amino Acid Esters and Peptides in 'Metal Ions in Biological Systems,' vol V, ed. H. Sigel, Marcel Dekker, New York, to be published.

[3] D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1968, **90**, 6032.

[4] M. D. Alexander and D. H. Busch, *J. Amer. Chem. Soc.*, 1966, **88**, 1130.

[5] D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1970, **92**, 6151.

[6] D. A. Buckingham, A. M. Sargeson, and A. Zanella, *J. Amer. Chem. Soc.*, 1972, **94**, 8246.

[7] D. Pinnell, G. B. Wright, and R. B. Jordan, *J. Amer. Chem. Soc.*, 1972, **94**, 6104.

[8] B. Hansen, *Acta Chem. Scand.*, 1963, **17**, 1307.

[9] R. B. Martin, R. I. Hedrick, and A. Parcell, *J. Org. Chem.*, 1964, **29**, 3197.

[10] G. L. Schmir, *J. Amer. Chem. Soc.*, 1968, **90**, 3478.

[11] M. Krishnamurthy, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3915.

[12] A. Werner, *Annalen*, 1912, **386**, 118.

[13] C. W. Crane and H. W. Rydon, *J. Chem. Soc.*, 1947, 527.

from acetone m.p. 131 (lit.[1] 132 °C). The complex *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OCOMe)]Cl_2$, containing the *N*-coordinated amino-alcohol ester, was prepared essentially as described by Alexander and Busch [14] for similar complexes of glycine methyl ester. The crude material was recrystallised from the minimum of water (60 °C). Crystallisation was initiated by addition of a few drops of hydrochloric acid (12M). The *complex* was dried *in vacuo* over silica gel (Found: C, 24·7; H, 6·5; N, 17·8. Calc. for $C_8H_{25}Cl_3CoN_5O_2$: C, 24·7; H, 6·5; N, 18·0%). The i.r. spectrum established that the complex was anhydrous. A strong band at 1 745 cm^{-1} in the complex can be assigned to ν(CO)(ester). The bromo-derivative was prepared similarly.

The complex *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OH)]Cl_2$ was prepared as previously described,[15] and the bromo-derivative by a similar method. Acid hydrolysis of *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OCOMe)]Cl$ gave the corresponding complex of 2-aminoethanol. The ester complex (1 g) was dissolved in the minimum volume of hydrochloric acid (*ca.* 6M) and the solution set aside. The product slowly crystallised during 3 days, and was recrystallised from the minimum of warm water containing a few drops of hydrochloric acid (12M). The i.r. spectrum was identical to that of the complex prepared directly from 2-aminoethanol (Found: C, 19·8; H, 6·7; N, 19·4. $[Co(en)_2Cl(NH_2CH_2CH_2OH)]Cl_2,H_2O$ requires C, 19·4; H, 6·9; N, 19·3%).

Kinetics and Measurements.—Ionisation constants and kinetics were measured with a Radiometer TTT1 automatic titrator, used in conjunction with a Radiometer PHA 630T scale expander. A high-alkalinity glass electrode, type G202B, was used as indicator electrode and a saturated calomel electrode with diffusion filter, type K401, as reference electrode. The electrode system was standardised at 25·0 °C with 0·05M-potassium hydrogenphthalate (pH 4·005) and disodium tetraborate (pH 9·185) buffers. The general technique employed in the kinetic measurements has been outlined.[16] All kinetic studies by pH-stat were carried out at $I = 0{\cdot}1$M (KCl) and 25 °C. Values of the hydroxide-ion concentrations were obtained from the pH, by use of a molar activity coefficient of 0·772,[17] and a value of $pK_W = 13{\cdot}9965$ at 25 °C.[18] Hydrogen ions are liberated when 2-aminoethyl acetate reacts in basic solution. The rate of hydrogen-ion production at 25 °C and $I = 0{\cdot}1$M (KCl) was studied over the pH region 8·5—9·0. Plots of log ($V_\infty - V_t$) against time were linear and values of k_{obs} were obtained from the gradients of such plots (Table 1). Within this pH range the function $k_{obs}/[OH^-]$ was effectively constant at $10{\cdot}1 \times 10^3$ l mol^{-1} min^{-1}. When the appropriate corrections were made for ionic-strength differences, the results were in reasonable agreement with those of Hansen.[8]

TABLE 1

Values of k_{obs} for the disappearance of 2-aminoethyl acetate in basic media at 25 °C and $I = 0{\cdot}1$M (KCl)

pH	$10^2 k_{obs}$ / min^{-1}	$10^{-3} k_{obs}/[OH^-]$ / l mol^{-1} min^{-1}
8·50	4·14	10·0
8·50	4·30	10·4
8·60	5·07	9·75
8·60	5·32	10·2
8·70	7·01	10·7
8·70	6·87	10·5
8·80	8·15	9·9
8·80	8·65	10·5
8·90	10·2	9·9
8·90	10·1	9·7
9·00	13·0	9·9
9·00	13·7	10·4

The spectrophotometric kinetics were carried out using a Gilford 2400S recording spectrophotometer. Base-hydrolysis kinetics were studied using carbonate–hydrogencarbonate buffers adjusted to $I = 0{\cdot}1$M. Mercury(II)-catalysed aquations were studied using $Hg(ClO_4)_2$–$HClO_4$ solutions. Visible spectra were measured with Perkin-Elmer 402 and Unicam SP 800 instruments.

RESULTS AND DISCUSSION

Base Hydrolysis.—Base hydrolysis of the complex *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OCOMe)]^{2+}$ was followed by pH-stat and spectrophotometry. Two consecutive or possibly concurrent reactions (3) and (4) could occur in basic media. Consistent with a kinetic scheme of this type it was found that two mol of base were consumed per mol of the complex (experimentally 2·03 ± 0·03 mol). Initial hydrolysis of the chloride ligand rather than the ester is consistent with the spectrophotometric kinetics (see later). Plots of log ($V_\infty - V_t$) against time (V_∞ is the final volume of base consumed and V_t the volume of base consumed at time t) showed marked initial curvature, becoming linear at high values of t (Figure 1). It was possible to resolve such plots into

$$cis\text{-}[Co(en)_2Cl(NH_2CH_2CH_2OCOMe)]^{2+} + OH^- \xrightarrow{k_{OH}^{Cl}} [Co(en)_2OH(NH_2CH_2CH_2OCOMe)]^{2+} \quad (3)$$

$$[Co(en)_2OH(NH_2CH_2CH_2OCOMe)]^{2+} + OH^- \xrightarrow{k_{OH}^{ester}} [Co(en)_2OH(NH_2CH_2CH_2OH)]^{2+} + MeCO_2^- \quad (4)$$

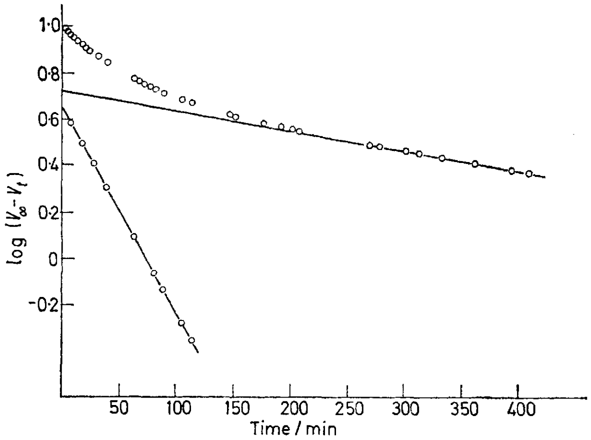

FIGURE 1 Base hydrolysis of the complex *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OCOMe)]^{2+}$, followed by pH-stat at pH 9·0, 25 °C, and $I = 0{\cdot}10$M, showing resolution into two consecutive reactions

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[14] M. D. Alexander and D. H. Busch, *Inorg. Chem.*, 1966, **5**, 602.

[15] R. W. Hay and P. L. Cropp, *J. Chem. Soc.* (*A*), 1969, 42.

[16] R. W. Hay, L. J. Porter, and P. J. Morris, *Austral. J. Chem.*, 1966, **19**, 1197.

[17] C. W. Davies, *J. Chem. Soc.*, 1938, 2093.

[18] R. A. Robinson and R. H. Stokes, ‘ Electrolyte Solutions,’ 2nd edn., Butterworths, London, 1965.

two straight lines by conventional procedures.[19] Such behaviour is consistent with two consecutive pseudo-first-order reactions at constant pH, as shown in equations (3) and (4). The pH-stat kinetic data is summarised in Table 2. The value of k_{OH}^{Cl} is $(1{\cdot}38 \pm 0{\cdot}06) \times 10^3$ l mol^{-1} min^{-1} at 25 °C and $I = 0{\cdot}1$M. Under these conditions $k_{OH}^{ester} = (1{\cdot}44 \pm 0{\cdot}10) \times 10^2$ l mol^{-1} min^{-1}. Base hydrolysis of the chloride ligand is therefore 10 times faster than that of the ester.

TABLE 2

Base hydrolysis of the complex *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OCOMe)]^{2+}$ at 25 °C and $I = 0{\cdot}1$M †

(*a*) pH-Stat kinetics

pH	10^2k_1(obs) / min^{-1}	$10^{-3}k_1$(obs)/[OH$^-$] / l mol^{-1} min^{-1}	10^3k_2(obs) / min^{-1}	$10^{-2}k_2$(obs)/[OH$^-$] / l mol^{-1} min^{-1}
8·92	1·43	1·35	1·52	1·44
9·42	4·64	1·38	4·84	1·44
9·71	8·86	1·36	9·82	1·50
10·02	15·1	1·44	15·7	1·51
10·37	*		40·9	1·36
10·66	*		81·5	1·40
		Av. 1·38 ± 0·06		Av. 1·44 ± 0·10

(*b*) Spectrophotometric kinetics (λ = 505 nm)

pH	10^2k_{obs} / min^{-1}	$10^{-3}k_{obs}$/(OH$^-$] / l mol^{-1} min^{-1}
9·40	4·61	1·44
9·45	4·98	1·40
9·60	7·35	1·45
9·71	9·00	1·35
		Av. 1·42 ± 0·04

* The reaction was too rapid to obtain precise constants.

† $k_1 \equiv k_{OH}^{Cl}$, $k_2 \equiv k_{OH}^{ester}$.

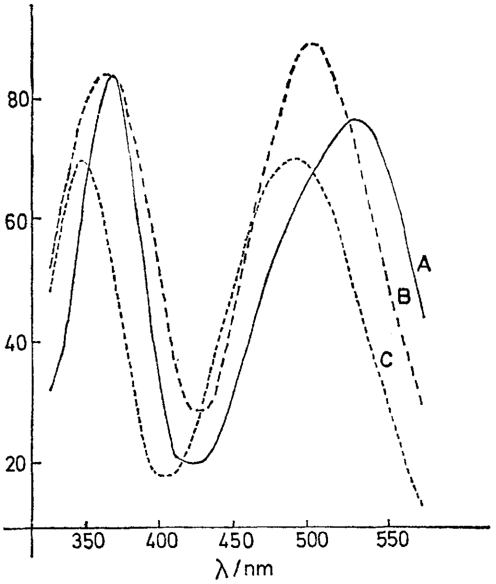

FIGURE 2 Electronic spectra of the complex *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OCOMe)]^{2+}$ and the products of base hydrolysis: (A) penta-aminechloro-complex; (B) product of base hydrolysis; and (C) product of base hydrolysis adjusted to pH 3

Conversion of the penta-aminechloro- to the penta-aminehydroxo-complex led to significant visible spectral changes owing to an alteration of the ligand field about the cobalt(III) ion. Thus an N_5Cl donor system has $\lambda_{max.}$ at *ca.* 527 ± 3 nm for the lowest-energy ligand-field band, compared with $\lambda_{max.}$ *ca.* 504 ± 3 nm for the $N_5(OH)$ donor system. Hydrolysis of the ester ligand should have no effect on the electronic spectrum as the ligand field is unaltered. Figure 2 illustrates the spectral changes observed on base hydrolysis of the complex *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OCOMe)]^{2+}$. These changes are consistent with conversion of the penta-aminechloro- to the penta-aminehydroxo-complex. Measurements in carbonate buffers indicated that a single rate process accounted for the visible spectral changes. Kinetic measurements were carried out at 25 °C and $I = 0{\cdot}1$M using 504 nm as the monitoring wavelength. Plots of log $[OD_\infty - OD_t]$ against time were linear for at least two half-lives. Spectrophotometric kinetic data is summarised in Table 2(*b*). The spectrophotometric rate constant, $k_{OH} = (1{\cdot}42 \pm 0{\cdot}04) \times 10^3$ l mol^{-1} min^{-1}, is in exact agreement with the ' fast ' pH rate constant $(1{\cdot}38 \pm 0{\cdot}06) \times 10^3$ l mol^{-1} min^{-1}, confirming that the initial fast hydrolytic reaction is due to base hydrolysis of the chloride ion.

A kinetic study was also carried out on base hydrolysis of the complex *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OH)]^{2+}$ under the same conditions of temperature and ionic strength. The rate constants obtained are summarised in Table 3. pH-Stat and spectrophotometric rate constants are in excellent agreement giving a value of $k_{OH} = (1{\cdot}24 \pm 0{\cdot}05) \times 10^3$ l mol^{-1} min^{-1} at $I = 0{\cdot}1$M and 25 °C. This constant is similar to the ' fast ' rate constant obtained for the 2-aminoethyl acetato-derivative, providing additional confirmatory evidence that the ' fast ' reaction is due to base hydrolysis of the chloride ion.

Hydrolysis of the penta-aminechloro-complex derived from 2-aminoethanol is some two times as fast as the

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[19] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanisms,' 2nd edn., John Wiley, London, 1961.

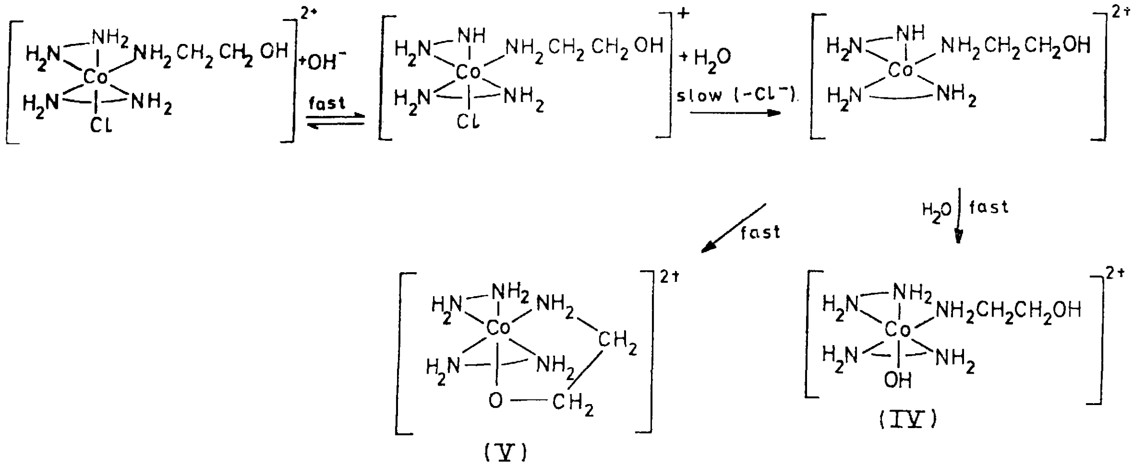
corresponding derivatives of ethylamine and *n*-propylamine,[15] a result which has been commented on by Chan and Leh.[20] Chan *et al.* have suggested [20,21] that spontaneous release of chloride ion from aqueous solutions of the *cis*-chlorobis(ethylenediamine)(2-hydroxyethylamine)cobalt(III) cation involves rate-determining internal attack on cobalt by an oxygen lone-pair in the unidentate 2-hydroxyethylamine ligand, assisting the expulsion of the co-ordinated chloride ligand. The resulting intermediate, in which 2-hydroxyethylamine acts as a chelate, then undergoes rapid one-end displacement of the chelate by a solvent molecule to form the aquobis(ethylenediamine)(2-hydroxyethylamine)cobalt(III) ion. Such a chelation mechanism could arise as the oxygen and nitrogen atoms in 2-aminoethanol are suitably spaced to form a five-membered chelate ring; however, cleavage of a chelate ring, once formed, would not be expected to be a very favourable process.

TABLE 3

Base hydrolysis of the complex $[Co(en)_2Cl(NH_2CH_2CH_2OH)]^{2+}$ at I = 0·1M and 25 °C

pH	10^2k_{obs} / min^{-1}	$10^{-3}k_{obs}$ / $l\,mol^{-1}\,min^{-1}$
(*a*) pH-Stat kinetics		
9·00	1·62	1·24
9·10	1·99	1·24
9·42	40·2	1·20
9·50	5·08	1·23
9·60	6·22	1·20
9·77	9·52	1·27
		Av. 1·23 ± 0·05
(*b*) Spectrophotometric kinetics *		
9·35	3·39	1·19
9·54	5·60	1·27
9·71	8·29	1·27
		Av. 1·24 ± 0·05

* Reaction monitored at 505 nm.



SCHEME 1

If, as appears probable,[22] base hydrolysis of the complex *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OH)]^{2+}$ occurs by an $S_N1(CB)$ mechanism in which the rate-determining step is loss of Cl^- from the amido-complex to give a five-co-ordinate intermediate, the hydroxy-group of 2-amino-ethanol can compete with water for the vacant co-ordination site in the five-co-ordinate intermediate (Scheme 1). Spectral changes observed on acidification of solutions of the complex *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OH)]^{2+}$ after base hydrolysis (Figure 2) are consistent with formation of the penta-aminehydroxo-complex rather than the chelated species (V).

The pK_a value for the equilibrium $[Co(en)_2OH_2(NH_2CH_2CH_2OH)]^{3+} \rightleftharpoons [Co(en)_2OH(NH_2CH_2CH_2OH)]^{2+} + H^+$ was determined spectrophotometrically at 500 nm and I = 0·1M and 25 °C (Table 5). The practical ionisation constant is pK_a^P = 6·08 ± 0·02 under these conditions and the thermodynamic value pK_a^T = 5·55, using molar activity coefficients calculated from the Davies equation.[17] Potentiometric titration gave a practical pK_a^P = 6·12 ± 0·02 under the same conditions of temperature and ionic strength. The clean isosbestic points at 426 and 466 nm and the constancy of the pK values are consistent with the view that (*a*) a single product, the penta-aminehydroxo-complex, is formed on base hydrolysis and (*b*) little, if any, configurational change of the *cis* $\rightleftharpoons$ *trans* type occurs. Poon [22] has reviewed the steric course of base hydrolysis of a number of cobalt(III)–amine complexes. For *cis*-complexes of the type $[Co(en)_2NH_3(X)]^{2+}$ (X = Cl or Br) some 85% of the product has the *cis*-configuration. We have also previously shown [15] that base hydrolysis of the complex *cis*-$[Co(en)_2Cl(NH_2Me)]^{2+}$ occurs with essentially complete retention of configuration.

For the complex *cis*-$[Co(en)_2Br(NH_2CH_2CH_2OH)]^{2+}$ k_{OH}^{Br} = 1·0 × 10^4 l mol^{-1} min^{-1} at 25 °C (Table 4) and for the 2-aminoethanol derivatives k_{OH}^{Br}/k_{OH}^{Cl} = 8·1.

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[20] S. C. Chan and F. Leh, *J. Chem. Soc.* (*A*), 1967, 1730.

[21] S. C. Chan and O. W. Lau, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3261.

[22] For a discussion see C. K. Poon, *Inorg. Chim. Acta Rev.*, 1970, **4**, 123.

Base hydrolysis of the complex *cis*-$[Co(en)_2Br(NH_2CH_2CH_2OCOMe)]^{2+}$ has also been studied. Base hydrolysis of the bromide ligand is usually some 6 times faster than that of chloride so that it is possible to study bromide and ester hydrolysis in isolation by appropriate adjustments of the pH of the solution. In the pH-stat measurements bromide hydrolysis was studied in the pH range 8·4—8·9 and the much slower ester hydrolysis in the range 10·3—10·6. The results obtained are shown in Table 4. At 25 °C and $I = 0{\cdot}1\text{M}$, $k_{OH}^{Br} = (8{\cdot}7 \pm 0{\cdot}3) \times 10^3$ l mol^{-1} min^{-1}, so that $k_{OH}^{Br}/k_{OH}^{Cl} = 6{\cdot}2$. The rate constant for ester hydrolysis $k_{OH} = 1{\cdot}5 \times 10^2$ l mol^{-1} min^{-1} is in close agreement with the value of $1{\cdot}4 \times 10^2$ l mol^{-1} min^{-1} obtained for hydrolysis of the penta-aminechloro-derivative. Spectrophotometric rate constants (Table 4) confirm that the 'fast' hydrolysis step is due to bromide hydrolysis.

TABLE 4

Base hydrolysis of penta-aminebromo-complexes *cis*-$[Co(en)_2Br(NH_2R)]^{2+}$ at $I = 0{\cdot}1\text{M}$ and 25 °C

pH	10^2k_{obs}/min^{-1}	$10^{-3}k_{OH}^{Br}$/l mol^{-1} min^{-1}
pH-Stat measurements		
R = CH_2CH_2OCOMe		
(*a*) Bromide hydrolysis		
8·40	2·85	8·9
8·70	5·38	8·5
8·85	7·96	8·8
(*b*) Ester hydrolysis		$10^{-2}k_{OH}^{ester}$/l mol^{-1} min^{-1}
10·30	3·86	1·5
10·45	5·44	1·5
10·56	7·50	1·6
R = CH_2CH_2OH		
Bromide hydrolysis		$10^{-3}k_{OH}^{Br}$/l mol^{-1} min^{-1}
8·32	2·62	9·8
8·57	4·78	10·2
8·78	7·37	9·7
Spectrophotometric rate constants obtained using borax buffers*		
R = CH_2CH_2OCOMe		
Bromide hydrolysis		
8·40	2·66	7·8
8·60	3·75	7·4
8·86	7·20	8·3
R = CH_2CH_2OH		
8·40	3·01	9·4
8·70	5·95	9·3
8·93	$9{\cdot}50_5$	8·8

* λ = 490 nm.

In the case of hydrolysis of the *cis*-$[Co(en)_2X(NH_2CH_2CH_2OCOMe)]^{2+}$ ions (X = Cl or Br) initial base hydrolysis of the halide ion occurs and possible reactions of the five-co-ordinate intermediate are shown in Scheme 2. It seems probable that the more basic carbonyl oxygen rather than the ether oxygen atom will co-ordinate preferentially in this case. The basicity of the ether oxygen atom of the ester linkage is depleted due to the resonance of the type shown below. Formation of the chelated intermediate (VI) would require formation of the less thermodynamically stable seven-membered chelate ring and would not appear to be very probable. The 'slow' rate

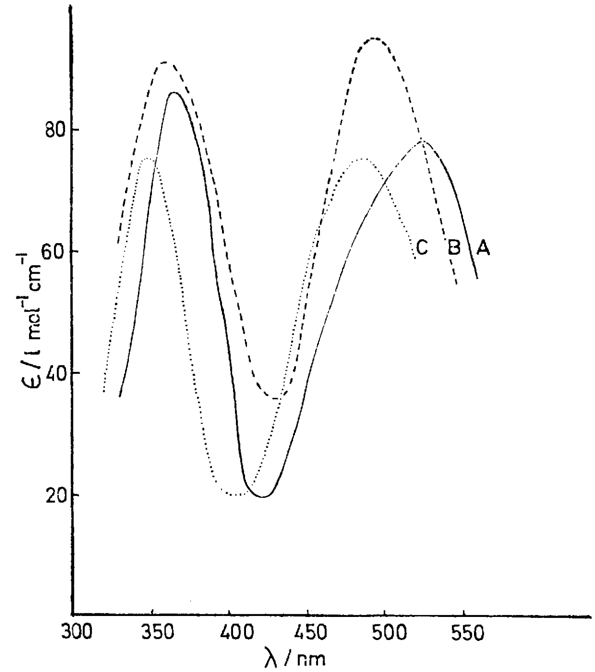


FIGURE 3 Electronic spectra of the complex *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OH)]^{2+}$ and the products of base hydrolysis: (A) penta-aminechloro-complex; (B) product of base hydrolysis; and (C) product of base hydrolysis adjusted to pH 3

TABLE 5

(*a*) Absorption spectra of $[Co(en)_2X(NH_2R)]^{n+}$ ions

	$\lambda_{max.}$*	ε†	$\lambda_{max.}$*	ε†
R = CH_2CH_2OH				
X = Cl	527	75	367	82
X = OH	500	89	362	87
X = OH_2	490	73	350	74
R = CH_2CH_2OCOMe				
X = Cl	527	72	368	79

(*b*) Spectrophotometric pK_a values of penta-aminehydroxo-complexes formed in base hydrolysis ‡

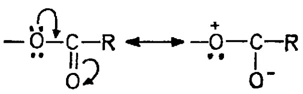
(i) Product obtained on complete base hydrolysis of *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OCOMe)]^{2+}$

pH	5·47	5·70	5·91	6·14	6·34	6·54	6·70
pK_a^P	6·03	6·06	6·09	6·06	6·10	6·10	6·10

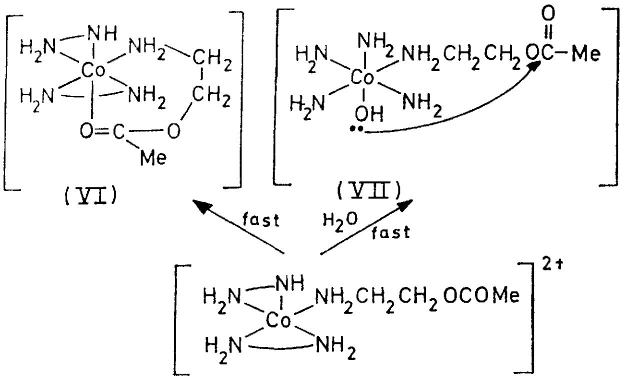
(ii) Product of base hydrolysis of *cis*-$[Co(en)_2Cl(NH_2CH_2CH_2OH)]^{2+}$

pH	5·39	5·02	5·82	6·10	6·29	6·50	6·70
pK_a^P	6·08	6·09	6·13	6·14	6·14	6·09	6·14

* In nm. † In l mol^{-1} cm^{-1}. ‡ Determined at $I = 0{\cdot}1\text{M}$ (KNO_3) and λ = 500 nm.



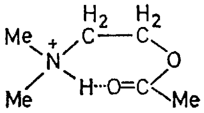
constant observed for base hydrolysis of the ester complex, 144 l mol^{-1} min^{-1}, may be compared with values estimated by Hansen[8] for the reactions (1) and (2) (k_{OH} *ca.* 180—300 and 6—9 l mol^{-1} min^{-1} respectively at $I = 0{\cdot}07$M and 25 °C). The above rate constants cannot be measured with precision due to complexities in the hydrolysis.



SCHEME 2

Base hydrolysis of choline acetate [equation (5)] has been subjected to detailed study. Bell and Robson[23] report a value of $k_{OH} = 76$ l mol^{-1} min^{-1} at 25 °C and $I = 0{\cdot}104$M (KBr). Investigations by Aksnes and Frøyen[24] have shown that esters such as $Me_2NHCH_2CH_2OCOMe$ undergo very rapid base hydrolysis, $k_{OH} = 2\,346$ l mol min^{-1}. The rapid base hydrolysis has been attributed to H-bonding catalysis which cannot occur with betaine methyl ester.

$$Me_3\overset{+}{N}CH_2CH_2OCOMe + OH^- \xrightarrow{k_{OH}} Me_3\overset{+}{N}CH_2CH_2OH + MeCO_2^- \quad (5)$$



Polarisation of the carbonyl group by hydrogen bonding presumably makes the carbonyl carbon atom more susceptible to nucleophilic attack. Hydrolysis of choline acetate is thus a better model for hydrolysis of the *N*-protonated form of 2-aminoethyl acetate if it is wished to isolate electrostatic effects from H-bonding effects.

Hydrolysis of the ester in the dipositive cobalt(III) complex is thus some 18 times faster than that for the free ligand and some two times as fast as for the protonated ligand. Such small rate enhancements exclude the occurrence of chelated ester of species such as (VI) which would lead[2] to rate enhancements of *ca.* 10^6. Intramolecular nucleophilic attack, as shown in (VII), can also be excluded on similar grounds (rate enhancements 10^6—10^9).[2]

Mercury(II)-*catalysed Aquation*.—Mercury(II)-catalysed aquations of the complexes *cis*-$[Co(en)_2X(NH_2CH_2CH_2OCOMe)]^{2+}$ (X = Cl or Br) and the corresponding derivative of 2-hydroxyethylamine were also studied. Mercury(II)-catalysed aquations are believed to proceed *via* five-co-ordinate intermediates[25] of a somewhat different type than occurs in S_N1(CB) base hydrolyses, and full retention of configuration occurs. The kinetic data obtained are summarised in Table 6. The reactions were studied spectrophotometrically and excellent pseudo-first-order plots were obtained at constant mercury(II) concentrations. Values of $k_{obs}/[Hg^{II}]$ were sensibly constant. For both the chloro- and bromo-complexes hydrolysis of the 2-aminoethanol derivative was considerably faster than that for the 2-aminoethyl acetate. At $I = 2{\cdot}07$M and $[HClO_4] = 0{\cdot}57$M k_{Hg} values are 3·52 and 0·48 l mol^{-1} min^{-1} (chloro-complexes) and 400 ± 25 and 68 ± 2 l mol^{-1} min^{-1} (bromo-complexes) at 25 °C. The seven-fold rate acceleration in the chloro-complex and the six-fold rate acceleration in the bromo-complex could be due to anchimeric assistance by the neighbouring hydroxy-group (NGP-5OH) in expulsion of the halide ion. Numerous examples of neighbouring participation by hydroxy-groups in organic systems are known.[26] Possibly the neighbouring hydroxy-group stabilises the five-co-ordinate intermediate, which, by

TABLE 6

Mercury(II)-catalysed aquations at 25 °C

$[Hg^{II}]$ M	k_{obs} min^{-1}	$k_{obs}/[Hg^{II}]$ l mol^{-1} min^{-1}
cis-$[Co(en)_2Cl(NH_2CH_2CH_2OCOMe)]^{2+}$		
0·1	0·049	0·49
0·2	0·098	0·49
0·3	0·142	0·47
0·4	0·172	0·43
0·5	0·239	0·48
$I = 2{\cdot}07$, $[HClO_4] = 0{\cdot}57$M, λ = 487 nm.		
cis-$[Co(en)_2Cl(NH_2CH_2CH_2OH)]^{2+}$		
0·02	0·043	2·15
0·04	0·087	2·18
0·06	0·130	2·16
0·08	0·162	2·03
0·10	0·205	2·05
$I = 0{\cdot}87$, $[HClO_4] = 0{\cdot}57$M, λ = 491 nm.		
cis-$[Co(en)_2Br(NH_2CH_2CH_2OCOMe)]^{2+}$		
$10^3[Hg^{II}]$ M		
1·0	0·069	69·3
1·6	0·106	68·6
3·2	0·220	66·0
$I = 2{\cdot}07$, $[HClO_4] = 0{\cdot}57$M, λ = 500 nm.		
cis-$[Co(en)_2Br(NH_2CH_2CH_2OH)]^{2+}$		
1·0	0·421	421
1·6	0·614	383
3·2	1·30	406
$I = 2{\cdot}0$, $[HClO_4] = 0{\cdot}57$M, λ = 500 nm.		

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[23] R. P. Bell and M. Robson, *Trans. Faraday Soc.*, 1964, **60**, 893.

[24] G. Aksnes and P. Frøyen, *Acta Chem. Scand.*, 1966, **20**, 1451.

[25] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Inorg. Chem.*, 1967, **6**, 1807.

[26] See for example, A. J. Kirby and A. R. Fersht in ' Progress in Bio-organic Chemistry,' vol. 1, eds. E. T. Kaiser and F. J. Kezdy, Wiley–Interscience, New York, 1971, p. 65.

Hammond's postulate,[27] must resemble the transition state for loss of the halide ion and thence the observed rate acceleration.

Visible spectra of the products of the Hg^{II}-catalysed aquations were identical to those of base hydrolysis after acidification, thus providing strong confirmatory evidence that base hydrolysis of these complexes occurs with essentially complete retention of configuration. It is improbable that the *cis*- and *trans*-penta-amine-aquo-complexes have identical absorption spectra.

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[3/1004 *Received*, 17*th May*, 1973]

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[27] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.