Amino-acid Complexes of Cobalt(III). Preparation and Hydrolysis Reactions of *trans*-Bis(1,2-diaminoethane)(amino-carboxylato)halogenocobalt(III) Complexes containing the Carboxylato-bonded Amino-acids Glycine, DL-Alanine, and DL-Aminobutyric Acid

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A series of complexes of the type *trans*-$[Co(en)_2X\{^-O_2C-CH(R)-NH_3^+\}][ClO_4]_2$ (X = Cl^- or Br^-), containing the monodentate carboxylato-bonded amino-acids, glycine (R = H), DL-alanine (R = Me), and DL-aminobutyric acid (R = Et) have been prepared and characterised. All the complexes behave as monobasic acids and pK_a values for the equilibrium (1) have been determined potentiometrically at 25 ± 0.1 °C. The kinetics and steric course of

$$trans\text{-}[Co(en)_2X\{^-O_2C-CH(R)-NH_3^+\}]^{2+} \overset{K_a}{\rightleftharpoons} trans\text{-}[Co(en)_2X\{^-O_2C-CH(R)-NH_2\}]^+ + H^+ \qquad (1)$$

base hydrolysis (X^- displacement) of the species *trans*-$[Co(en)_2X\{^-O_2C-CH(R)-NH_2\}]^+$ have been examined. Values of $\Delta H^\ddagger$(298.15) lie between 92.9 and 96.6 kJ mol^{-1} for all the complexes studied. Values of $\Delta S^\ddagger$(298.15) for the chloro-complexes lie in the region 76—87 J K^{-1} mol^{-1} and for the bromo-complexes in the region 92—101 J K^{-1} mol^{-1}. Base hydrolysis of the DL-alanine and DL-aminobutyric complexes give 65 ± 5% *trans*- and 35 ± 5% *cis*-$[Co(en)_2OH\{^-O_2C-CH(R)-NH_2\}]^+$. The products of base hydrolysis of the glycine complexes contain in addition minor quantities of the *N*-bonded complex $[Co(en)_2OH(NH_2CH_2CO_2^-)]^+$. The kinetics and steric course of the Hg(II)-assisted aquation of the complexes *trans*-$[Co(en)_2X\{^-O_2C-CH(R)-NH_3^+\}]^{2+}$ have also been studied. For the chloro-complexes $\Delta H^\ddagger$(298.15) values of 80.9—82.2 kJ mol^{-1} and $\Delta S^\ddagger$(298.15) values of 0.96—4.8 J K^{-1} mol^{-1} have been obtained, while for the bromo-complexes $\Delta H^\ddagger$(298.15) values lie in the range 74.6—75.4 kJ mol^{-1} with $\Delta S^\ddagger$(298.15) values in the range 28—35 J K^{-1} mol^{-1}. The products of this reaction are 85 ± 5% *cis*-, 15 ± 5% *trans*-$[Co(en)_2OH_2\{^-O_2C-CH(R)-NH_3^+\}]^{3+}$.

THE reactions between various classes of amines and *trans*-$[Co(en)_2X_2]^+$ cations (X = Cl^- or Br^-; en = 1,2-diaminoethane) have been widely investigated since first reported by Meisenheimer,[1] and the courses taken by these reactions have recently been reviewed.[2] Surprisingly the reactions between *trans*-$[Co(en)_2X_2]^+$ and amino-acids have received relatively scant attention. Nevertheless treatment of the dichloro-complex with some optically active amino-acids (AA), in the presence of equimolar amounts of base, was found to give on heating the optically active complexes $[Co(en)_2(AA)]^{2+}$, in which the amino-acids fulfill their customary bidentate roles.[3] Reactions between *trans*-$[Co(en)_2X_2]^+$ and amino-acid esters,[4,5] AE, and amides [6] AAm, give the products *cis*-$[Co(en)_2X(AE)]^{2+}$ and *cis*-$[Co(en)_2X(AAm)]^{2+}$, respectively, in which the ester and amide ligands are both monodentate and amino-bonded to the metal ion. Hydrolysis reactions of the complexes have been investigated and in the case of the glycine ester [7,8] and glycinamide [6] complexes additional reactions have been reported. These involve incorporation of carbonyl groups into the vacant co-ordination sites of five-co-ordinate cobalt(III) intermediates as well as intramolecular reactions between juxtaposed ester or amide groups and the hydroxy-ligands in the hydrolysis products. Some *N*-bonded monodentate amino-acid complexes, *cis*-$[Co(en)_2Cl(AA)]^{2+}$, have also been prepared by hydrolysis of the corresponding ester complexes in hydrochloric acid solutions.[5]

We have recently commenced investigations into the reactions of amino-acids with *trans*-$[Co(en)_2X_2]^+$ and have found that under weakly basic conditions, complexes of the type *trans*-$[Co(en)_2X(AA)]^{2+}$, in which the amino-acid is monodentate and bonded through its carboxylate group to the metal ion, are formed. In this paper we report the preparation and characterisation of the glycine, DL-alanine, and DL-aminobutyric acid complexes as well as rate data for their hydrolysis reactions.†

EXPERIMENTAL

Materials.—*trans*-$[Co(en)_2Cl_2][Cl]$ was prepared by the literature method.[9] *trans*-$[Co(en)_2Br_2][Br]$ was prepared by dissolving *trans*-$[Co(en)_2Cl_2][Cl]$ in hot (80 °C) concentrated HBr, cooling the solution in an ice-bath, and heating the crystalline product thus obtained in an oven at 120 °C. The complexes *trans*-$[Co(en)_2X\{^-O_2C-CH(R)-NH_3^+\}][ClO_4]_2$ (X = Cl^- or Br^-; R = H, Me, or Et) were prepared as follows. *trans*-$[Co(en)_2X_2][X]$ (0.01 mol) and the amino-acid (0.01 mol) were ground together and made into a paste by the addition of a little water. Diethylamine (*ca.* 0.2 cm^3) was added dropwise with continuous grinding to the paste until the colour change was complete (mauve in the case of the chloro-complexes, dark green in the case of the bromo-complexes). The mixture was then treated with 0.5 mol dm^{-3} $HClO_4$ (20 cm^3) and heated on a steam-bath until most of the solid material had dissolved. This was filtered while hot and the filtrate then treated with concentrated $HClO_4$ (1 cm^3). On cooling, the complexes crystallised as mauve (chloro-complexes) or dark green (bromo-complexes) needles. All complexes were recrystallised from 1 mol dm^{-3} $HClO_4$ and were obtained in 60—80% yields. Analytical data for the complexes are given in Table 1.

† *Note added at proof:* We have now prepared a series of isomeric *O*- and *N*-bonded monodentate amino-acid complexes $[Co(en)_2Cl(AA)]^{2+}$ where AA = glycine, β-alanine, γ-aminobutyric acid, or ε-aminohexanoic acid (K. B. Nolan and A. A. Soudi, *J. Chem. Res.* (*S*), 1979, **6**, 210). Branched chain α-amino-acids do not form *N*-bonded complexes under the conditions described in this reference.

Potentiometric and Spectrophotometric Measurements.—The i.r. spectra of the complexes were recorded as Nujol mulls between NaCl plates in the range 600—4 000 cm^{-1} on a Perkin-Elmer 577 spectrophotometer. Electronic solution spectra were obtained using Unicam SP 8000 and 3000 spectrophotometers. Kinetics of hydrolysis reactions were followed spectrophotometrically by monitoring the absorbance increase at 512 nm (base hydrolysis) or 498 nm [Hg(II)-assisted aquation] on a Unicam SP 1800 spectrophotometer. The reaction solution [Hg(II)–HNO_3–$NaNO_3$ or NaOH–$NaClO_4$] was placed in the thermostatted cell compartment of the spectrophotometer and allowed to temperature-equilibrate for 20 min, after which time 10 μl of a concentrated aqueous solution of the complex were added. Proton ionisation constants of the complexes were determined potentiometrically using a Radiometer pH Meter 26. The electrode system (a high-alkalinity glass electrode, type G202B, and a saturated calomel electrode with a diffusion filter, type K401) was standardised at 298.2 ± 0.1 K with 0.05 mol dm^{-3} potassium hydrogenphthalate (pH 4.008) and 0.01 mol dm^{-3} borax (pH 9.185) buffers.[10] Titrations were performed in a vessel fitted with a cover which accommodated the electrode system, a thermometer, a nitrogen bleed, and a microburette from which alkali was added.

RESULTS AND DISCUSSION

Characterisation of Complexes.—Salient i.r. and electronic (350—700 nm) spectral features of the complexes are presented in Table 2. The i.r. spectra of the complexes show a sharp C=O stretching band at 1 630—1 640 cm^{-1} consistent with the presence in the complexes of co-ordinated carboxylate groups.[11,12] The complexes also show deformation bands due to the NH_3^+ groups in the 1 500 cm^{-1} region.

All three chloro-complexes show three bands in their electronic solution spectra in the 350—700 nm range with $\lambda_{max.}$ values at 575—580, 444—446, and 366—368 nm. This is fully consistent with a configuration in which Cl^- and the amino-acid occupy *trans* positions. Low-spin regular octahedral cobalt(III) complexes generally show two bands in this region due to the $^1A_{1g}\rightarrow{}^1T_{1g}$ (lower energy) and $^1A_{1g}\rightarrow{}^1T_{2g}$ transitions.[13] In complexes of the type *trans*-$[Co(en)_2(A)(B)]^{n+}$, where A and B are relatively weak-field ligands, the lower-energy band is resolved into two components due to splitting of the $^1T_{1g}$ state, and these complexes therefore show three bands in their visible and near-u.v. spectra. However, in the *cis* isomers splitting of the $^1T_{1g}$ state is much weaker and the bands corresponding to transitions from the ground state to the split excited states partly overlap. Consequently, the spectra of *cis* complexes consist of only two bands in this region. In the bromo-complexes the lowest-energy band occurs at longer wavelengths (by some 20 nm) than the corresponding band in the chloro-complexes, consistent with Br^- being lower in the spectrochemical series than Cl^-. The shortest-wavelength band in the bromo-complexes, however, is obscured by an intense charge-transfer band,[14] upon which the middle *d–d* band appears as a shoulder. The molar absorption coefficient of the lowest-energy band also supports a *trans* assignment. *trans*-Complexes normally have molar absorption coefficients of 40—50 dm^3 mol^{-1} cm^{-1} for this band, whereas the values for *cis*-complexes are greater (70—80 dm^3 mol^{-1} cm^{-1}) due to a reduction in symmetry.[2] The low molar absorption coefficients (*ca.* 30 dm^3 mol^{-1} cm^{-1}) observed for the middle *d–d* bands seems to be a characteristic feature of co-ordinated carboxylate. Comparable values have been reported for *trans*-chloro(acetato)-, *trans*-bis(carboxylato)-,[15] and *trans*-aquacarboxylato-complexes.[16]

TABLE 1

Analytical data (%) for the complexes $[Co(en)_2X\{^-O_2C-CH(R)-NH_3^+\}][ClO_4]_2\cdot nH_2O$

			Found			Calc.		
R	X	*n*	C	H	N	C	H	N
H	Cl	0	14.6	4.4	14.2	14.8	4.3	14.3
	Br	0	13.7	3.9	12.6	13.5	4.0	13.1
Me	Cl	0	16.9	4.4	13.6	16.7	4.6	13.9
	Br	0	15.6	4.2	12.5	15.4	4.2	12.8
Et	Cl	1	18.0	4.7	12.8	18.0	5.1	13.1
	Br	0	16.6	4.4	12.1	17.1	4.5	12.5

TABLE 2

Electronic and i.r. spectral data for the complexes $[Co(en)_2X\{^-O_2C-CH(R)-NH_3^+\}][ClO_4]_2$

R	X	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})	ν(C=O)/cm^{-1}
H	Cl	575 (51.0), 446 (34.0), 367 (64.4)	1 640
	Br	598 (49.7), 450 (33.2)	1 640
Me	Cl	580 (46.5), 444 (32.7), 368 (63.8)	1 635
	Br	598 (55.6), 448 (29.2)	1 637
Et	Cl	578 (49.3), 444 (29.5), 366 (57.2)	1 637
	Br	599 (48.1), 450 (27.9)	1 635

The i.r. spectra of the complexes in the 850—900 cm^{-1} region, where Baldwin[17] has suggested that the most consistent differences between *cis*- and *trans*-bis(1,2-diaminoethane)cobalt(III) isomers occurs, show a single CH_2 (en) rocking band. This is consistent with a *trans* configuration since *cis*-complexes display a split absorption for this vibration.

Acidic Behaviour.—All the complexes reported in this publication behave as monobasic acids and consume one mol of alkali per mol of complex in the pH range 7—10 after allowing for base consumption due to base hydrolysis. This is consistent with the presence in these complexes of carboxylato-bonded amino-acids with protonated amino-groups for which pK_a values of *ca.* 8 would be expected[18] rather than *N*-bonded amino-acids with unionized carboxylic acid groups, which should have pK_a values <4.[19] The pK_a values for the ionisation (1)

$$trans\text{-}[Co(en)_2X\{^-O_2C-CH(R)-NH_3^+\}]^{2+} \overset{K_a}{\rightleftharpoons} trans\text{-}[Co(en)_2X\{^-O_2C-CH(R)-NH_2\}]^+ + H^+ \quad (1)$$

were obtained by standard potentiometric methods[20] although pH readings obtained during the final stages of neutralisation were not considered in the calculations because of interference from base hydrolysis at pH >9. The mixed pK_a values (involving hydrogen-ion *activities*, but *concentrations* of conjugate acids and bases) thus obtained at 298.2 ± 0.1 K and at ionic strength 1.0 mol dm^{-3} ($NaClO_4$) are presented in Table 3.

TABLE 3

pK_a Values for ionization of the complexes *trans*-[Co(en)$_2$X{$^-O_2C-CH(R)-NH_3^+$}]$^{2+}$ at 298.2 ± 0.1 K, and ionic strength 1.0 mol dm^{-3}

R	X	pK_a *
H	Cl	8.87
	Br	8.66
Me	Cl	8.79
	Br	8.68
Et	Cl	8.80
	Br	8.65

* All values ±0.03.

As expected, ionisation of the $-NH_3^+$ group has little effect on the visible–near-u.v. spectra of the complexes.

Base Hydrolysis.—In alkaline solutions the complexes *trans*-[Co(en)$_2$X{$^-O_2C-CH(R)-NH_3^+$}]$^{2+}$ which exist as conjugate acid-base equilibrium mixtures undergo reactions characterised by marked spectral changes. In all cases the lowest- and intermediate-energy *d–d* bands disappear and are replaced by a new band of greater intensity at 510 nm. The charge-transfer band in the near-u.v. spectra of the bromo-complexes disappears, indicative of a process involving removal of Br$^-$ from the complex. Well defined isobestic points were observed during the reactions, at 566 and 354 for the chloro-complexes and at 566 and 438 nm for the bromo-complexes. The observed spectral changes in all the reactions were shown to correspond to the release of one mol of halide ion per mol of complex by silver nitrate titrations on the acidified product-containing solutions. The spectra of the products obtained from the bromo-complexes were found to be similar to those obtained from the corresponding chloro-complexes. The above evidence is consistent with the occurrence of base hydrolysis. At high pH (>12) the complexes exist almost completely in their conjugate-base forms, *trans*-[Co(en)$_2$X{$^-O_2C-CH(R)-NH_2$}]$^+$. The kinetics of base hydrolysis of these species [equation (2)] were investigated

$$trans\text{-}[Co(en)_2X\{^-O_2C-CH(R)-NH_2\}]^+ + OH^- \longrightarrow [Co(en)_2OH\{^-O_2C-CH(R)-NH_2\}]^+ + X^- \quad (2)$$

spectrophotometrically under pseudo-first-order conditions ([OH$^-$]/[complex] = 30—120), by monitoring the absorbance increases, at 512 nm, of solutions of the complexes in 0.01—0.04 mol dm^{-3} NaOH. All solutions were adjusted to an ionic strength of 1 mol dm^{-3} using NaClO$_4$ as the supporting electrolyte. Plots of log ($A_\infty - A_t$) (where A_∞ and A_t are the absorbancies after 10 half-lives and at time *t*, respectively) *vs.* time *t* were linear for three half-lives. Values of $k_{obs.}$/[OH$^-$], (=k_2, Table 4), were found to be reasonably constant in this pH range at each temperature investigated. Activation parameters, $\Delta H^\ddagger$(298.15) and $\Delta S^\ddagger$(298.15) for base hydrolysis of each complex are listed in Table 5. It has been pointed out that enthalpies of activation for base hydrolysis of complexes of the type [Co(en)$_2$(A)Cl]$^{2+}$ are less sensitive than the rate constant to the nature of A, and usually fall in the region of 96 kJ mol^{-1}.[21] The values of $\Delta H^\ddagger$ for the chloro-complexes described in this publication are in agreement with this claim.

Steric Course.—Tobe[15] has recently investigated the steric course of hydrolysis of the acetato-complex *trans*-[Co(en)$_2$Cl(MeCO$_2$)]$^+$ and a spectrophotometric analysis of the products of base hydrolysis after acidification indicated the presence of a mixture containing 80% *trans* and 20% *cis*-[Co(en)$_2$(H$_2$O)(MeCO$_2$)]$^{2+}$. We have examined the products of base hydrolysis of the *trans*-[Co(en)$_2$X{$^-O_2C-CH(R)-NH_3^+$}]$^{2+}$ complexes by a similar method. Using the spectra of various mixtures of the isomers *cis*- and *trans*-[Co(en)$_2$(H$_2$O){$^-O_2C-CH(R)-NH_3^+$}]$^{3+}$ for comparison, base hydrolysis of the DL-alanine (R = Me) and the DL-aminobutyric acid (R = Et) complexes in 0.1 mol dm^{-3} NaOH were found to give after acidification solutions containing 65 ± 5% *trans* and 35 ± 5% *cis*-[Co(en)$_2$(H$_2$O){$^-O_2C-CH(R)-NH_3^+$}]$^{3+}$. Similar treatment of the glycine complexes, however, gave not only the *cis*- and *trans*-[Co(en)$_2$(H$_2$O)($^-O_2C-CH_2-NH_3^+$)]$^{3+}$ isomers in solution, but also the *N*-bonded amino-acid complex [Co(en)$_2$(H$_2$O)(NH$_2$CH$_2$CO$_2$H)]$^{3+}$. Interestingly, when a concentrated solution of the base-hydrolysis products of *trans*-[Co(en)$_2$Cl($^-O_2CCH_2NH_2$)]$^+$ was acidified with concentrated HCl some *cis*-[Co(en)$_2$Cl(NH$_2$CH$_2$CO$_2$H)]$^{2+}$, presumably an anation product of the complex *cis*-[Co(en)$_2$(H$_2$O)(NH$_2$CH$_2$CO$_2$H)]$^{3+}$, was isolated from solution. Back-titration of a solution of *trans*-[Co(en)$_2$Cl{$^-O_2CCH_2$-NH_3^+}]$^{2+}$ in 0.1 mol dm^{-3} NaOH indicated that the major products of base hydrolysis are *cis*- and *trans*-[Co(en)$_2$(OH)($^-O_2CCH_2NH_2$)]$^+$, both of which consume acid at

TABLE 4

Rate data for base hydrolysis of *trans*-[Co(en)$_2$X{$^-O_2C-CH(R)-NH_2$}]$^+$ complexes at various temperatures, at ionic strength 1.0 mol dm^{-3}

X	R	*T*/K	10^3[OH$^-$]/mol dm^{-3} ($10k_2$/dm^3 mol^{-1} s^{-1})
Cl	H	278.6	36.2 (2.47), 17.0 (2.49), 7.40 (2.43)
		288.4	36.2 (11.0), 17.0 (10.5), 7.40 (11.7)
		298.5	36.2 (41.4), 17.0 (40.1), 7.40 (38.5)
Br	H	273.8	36.2 (4.79), 17.0 (4.50), 8.33 (4.54)
		283.3	35.4 (21.8), 17.0 (21.8), 7.40 (21.2)
		293.0	35.4 (79.0), 16.3 (79.1), 6.80 (78.8)
Cl	Me	279.0	37.5 (1.67), 18.0 (1.68), 8.30 (1.69)
		288.1	37.5 (6.56), 18.0 (6.33), 8.30 (6.43)
		298.1	37.5 (24.7), 18.0 (26.4), 8.30 (26.4)
Br	Me	279.6	37.5 (9.76), 18.0 (9.67), 8.30 (9.36)
		288.1	37.5 (30.9), 18.0 (32.4), 8.30 (31.7)
		297.3	37.5 (114), 18.0 (117), 8.30 (111)
Cl	Et	279.5	37.5 (2.25), 18.0 (2.21), 8.30 (2.23)
		288.5	37.5 (7.25), 18.0 (7.06), 8.30 (6.99)
		297.1	35.2 (25.7), 16.2 (25.4), 6.66 (25.1)
Br	Et	280.1	37.5 (10.3), 18.0 (10.0), 8.30 (10.0)
		288.5	35.2 (38.6), 18.0 (36.9), 8.30 (35.9)
		296.6	37.5 (97.9), 16.2 (101), 6.66 (103)

TABLE 5

Second-order rate constants and activation parameters for base hydrolysis of the complexes *trans*-[Co(en)$_2$X-{$^-O_2C-CH(R)-NH_2$}]$^+$ at 298.15 K and ionic strength 1.0 mol dm^{-3}

R	X	k_2/dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
H	Cl	3.94	94.5	84
	Br	16.3	96.2	101
Me	Cl	2.62	96.6	87
	Br	12.7	94.6	93
Et	Cl	2.82	92.9	76
	Br	12.9	94.1	92

pH *ca.* 9 and *ca.* 6, due to protonation of the basic NH_2 group and the hydroxy-ligand, respectively. An inflection is observed in the titration curve below pH 5, and further consumption of acid below pH 3 is due to protonation of the carboxylate group in the *N*-bonded amino-acid complex $[Co(en)_2(OH_2)(NH_2CH_2CO_2^-)]^{2+}$. The titration results indicate that the complex $[Co(en)_2(OH)(NH_2CH_2CO_2^-)]^+$ constitutes $<10\%$ of the base hydrolysis product mixture. The data are, surprisingly, inconsistent with the presence of any chelated glycinate complex $[Co(en)_2(^-O_2CCH_2NH_2)]^{2+}$ among the reaction products.† The formation of the *N*-bonded glycinate complex in basic solution is not surprising, in view of the likelihood of the NH_2 group competing with H_2O for the vacant co-ordination site of the five co-ordinate Co(III) intermediate in base hydrolysis.

In all cases similar product mixtures were obtained from the chloro- and bromo-reactant complexes, in agreement with the generally accepted view that the steric course of base hydrolysis of Co(III) complexes is independent of the nature of the leaving group.[22] Base hydrolysis of the bromo-complexes proceed some 4—5 times faster than that of the corresponding chloro-complexes. In addition, amino-acid replacement reactions from the complexes *trans*-$[Co(en)_2X\{^-O_2C\text{-}CH(R)\text{-}NH_2\}]^+$ were not observed in any case. This is in agreement with the generally observed[2] order of lability of ligands in Co(III) complexes, *i.e.* $Br^- > Cl^- > R\text{-}CO_2^-$ (monodentate).

In solutions of pH <6.5 the complexes under investigation exist almost completely in their conjugate acid forms, *trans*-$[Co(en)_2X\{^-O_2C\text{-}CH(R)\text{-}NH_3^+\}]^{2+}$. At 298.2 K and $I = 1.0$ mol dm^{-3} ($NaClO_4$), base hydrolysis of these species (investigated spectrophotometrically using ' Hepes ' buffer) are between 13 ($X = Cl^-$, R = H) and 20 ($X = Cl^-$, R = Me) times more rapid than their corresponding conjugate bases, *trans*-$[Co(en)_2X\{^-O_2C\text{-}CH(R)\text{-}NH_2\}]^+$. The enhanced reactivity of the dipositively charged species is probably due to the amine ligands in these complexes being more acidic than those in the unipositively charged complexes. Consequently amido-conjugate-base formation, as required in an S_N1CB mechanism, is more greatly facilitated in the former case. The observed rate enhancements indicate that this effect overrides the expected weaker labilising effect of the ligand $^-O_2C\text{-}CH(R)\text{-}NH_3^+$ [relative to $^-O_2C\text{-}CH(R)\text{-}NH_2$] on the amido-conjugate-base, with respect to loss of X^-, in the rate-determining step of base hydrolysis.

Hg(II)-*assisted Aquation*.—In nitric acid * solutions containing Hg(II) the complexes *trans*-$[Co(en)_2X\{^-O_2C\text{-}CH(R)\text{-}NH_3^+\}]^{2+}$ undergo Hg(II) assisted aquation. The spectral changes associated with these reactions involve the replacement of the lower and medium energy *d–d* bands by a new band of greater intensity at 498 nm, the disappearance of the charge-transfer band in the near-u.v. spectra of the bromo-complexes, and well defined isosbestic points at 558, 433, 382, and 337 nm in reactions of the chloro-complexes and at 561 and 434 nm in reactions of the bromo-complexes.

The kinetics of these reactions were investigated by monitoring the absorbance changes at 498 nm. All reactions were studied at a constant ionic strength of 1.7 mol dm^{-3}, adjustment to this value when necessary being performed by the addition of an appropriate amount of $NaNO_3$. Hg(II) concentrations in all cases were vastly greater (50—100 times) than substrate concentrations. Values of $k_{obs.}/[OH^-]$, ($= k_2$), at various Hg(II) concentrations and at various temperatures are summarised in Table 6. Activation parameters $\Delta H^‡(298.15)$ and $\Delta S^‡(298.15)$ for all complexes investigated are presented in Table 7. The bromo-complexes undergo Hg(II)-

TABLE 6

Rate data for the Hg(II)-assisted aquation of the complexes *trans*-$[Co(en)_2X\{^-O_2C\text{-}CH(R)\text{-}NH_3^+\}]^{2+}$ at various temperatures, and at ionic strength 1.7 mol dm^{-3}, $[H^+] = 0.5$ mol dm^{-3}

X	R	T/K	10[Hg(II)]/mol dm^{-3} (10^3k_2/dm^3 mol^{-1} s^{-1})
Cl	H	279.1	3.90 (4.87), 1.95 (5.08), 0.98 (5.00)
		287.7	3.90 (15.5), 1.95 (15.5), 0.98 (14.2)
		297.5	3.90 (52.3), 1.95 (53.8), 0.98 (51.2)
		307.9	3.90 (144), 1.95 (137), 0.98 (142)
Br	H	273.8	3.70 (935), 1.80 (944), 0.93 (933)
		278.4	0.94 (1 590), 0.47 (1 690)
		283.3	0.46 (2 910), 0.23 (2 910)
Cl	Me	277.9	4.00 (3.03), 2.00 (3.01), 1.00 (2.98)
		288.0	4.84 (12.9), 2.13 (12.8), 1.06 (12.4)
		297.8	2.13 (30.7), 1.59 (31.6), 1.06 (33.4)
		308.5	2.13 (120), 1.59 (122), 1.06 (118)
Br	Me	274.1	1.90 (705), 0.95 (695), 0.48 (700)
		279.6	0.95 (1 420), 0.48 (1 370), 0.24 (1 300)
		285.1	0.95 (2 550), 0.48 (2 600), 0.24 (2 680)
Cl	Et	287.2	4.00 (11.2), 2.00 (10.8), 1.00 (11.1), 0.50 (11.3)
		298.1	2.00 (45.6), 1.00 (46.3), 0.50 (46.8), 0.25 (47.6)
		309.2	2.00 (160), 1.00 (161), 0.50 (158), 0.25 (167)
		318.8	2.00 (364), 1.00 (367), 0.50 (366), 0.25 (368)
Br	Et	273.7	2.00 (750), 1.00 (779), 0.50 (760), 0.25 (760)
		278.0	2.00 (1 300), 1.00 (1 280), 0.50 (1 310), 0.25 (1 290)
		282.7	1.00 (2 250), 0.50 (2 280), 0.25 (2 260), 0.13 (2 200)

TABLE 7

Second-order rate constants and activation parameters for the Hg(II)-assisted aquation of *trans*-$[Co(en)_2X\{^-O_2C\text{-}CH(R)\text{-}NH_3^+\}]^{2+}$ complexes at 298.15 K and ionic strength 1.7 mol dm^{-3}

R	X	k_2/dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
H	Cl	0.051	80.9	1.8
	Br	14.9	74.8	28
Me	Cl	0.037	81.5	1.0
	Br	11.1	75.4	28
Et	Cl	0.044	82.2	4.8
	Br	12.3	74.6	35

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† We have recently found, however, that this complex undergoes slow glycinate ring-opening in alkaline solutions (pH >13) to give *cis*-$[Co(en)_2(OH)(NH_2CH_2CO_2^-)]^+$ (*N*-bonded) and other products.

* The complexes were difficult to dissolve in perchloric acid.

assisted aquation some 250—300 times faster than the corresponding chloro-complexes at 25 °C. Rate ratios of comparable magnitude have been reported for a range of other Co(III)–halogenoamine systems.[2]

The products of the Hg(II)-assisted aquations were examined spectrophotometrically, as described for base hydrolysis, and found to be mixtures containing $85 \pm 5\%$ *cis*- and $15 \pm 5\%$ *trans*-$[Co(en)_2(H_2O)\{^-O_2C\text{-}CH(R)\text{-}NH_3^+\}]^{3+}$.* Titrations of the product solutions with ' Hepes ' buffer [which prevents precipitation of Hg(II) at higher pH] confirmed that *N*-bonded amino-acid complexes were not formed in these reactions.

Tobe *et al.*[15] have investigated the Hg(II)- and $[HgCl]^+$-promoted aquation of the acetato-complex *trans*-$[Co(en)_2Cl(O_2CMe)]^+$ and have reported a second-order rate constant of 0.4 $dm^3\ mol^{-1}\ s^{-1}$ for the overall catalytic process at 39.0 °C. We have compared the reactivities of the complexes *trans*-$[Co(en)_2Cl(^-O_2C\text{-}CH_2\text{-}NH_3^+)]^{2+}$ and *trans*-$[Co(en)_2Cl(O_2CMe)]^+$ under the same conditions and have found that the latter complex undergoes Hg(II)-assisted aquation some five times faster at 25 °C. Promotion of halide loss by Hg(II) has been explained in terms of rapid pre-equilibrium formation (equilibrium constant, K), of a halide-bridged complex, $^-Co(III)\text{-}X\text{-}Hg(II)^-$, followed by loss of the good leaving group $[HgX]^+$ in a dissociative activation process (rate constant, k_2').[23] Usually $K[Hg(II)] \ll 1$ and second-order kinetics are observed $\{rate = k_2'K[Hg(II)][substrate]\}$. The introduction of the electronegative substituent NH_3^+ into the non-participating acetate ligand should weaken the bridging capacity of co-ordinated Cl^- and hence reduce K. In addition, a reduction in k_2' would also be expected, since the labilising effect of a ligand in reactions of this type depends on the extent of charge donation to the reaction centre and hence should decrease with decreasing basicity of the ligand. Since glycine ($^+NH_3\text{-}CH_2\text{-}CO_2^-$) is much less basic than acetate, $\Delta\ pK_b = 2.5$ at 25 °C,[24] its labilising ability should also be lower. Since in all our experiments Hg(II) concentrations greatly exceeded substrate (and therefore $[HgCl]^+$) concentrations we did not investigate catalysis by $[HgCl]^+$.

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* The spectra of these kinetically controlled equilibrium mixtures undergo subsequent slow changes as the thermodynamically controlled compositions ($80 \pm 5\%$ *cis*, $20 \pm 5\%$ *trans*) are approached; at the Hg(II) concentrations used Hg(II)-assisted aquations are much faster than isomerisation of the aqua-products.

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