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The Kinetics and Stereochemistry of Spontaneous Aquation of *trans*-$[Co(en)_2N_3(Me_2SO)]^{2+}$, $[Co(en)_2N_3(DMF)]^{2+}$, $[Co(en)_2N_3Br]^+$ and $[Co(en)_2N_3Cl]^+$

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The syntheses of the new trans-*solvento complexes* trans-$[Co(en)_2(sol)N_3](ClO_4)_2$ *(sol =* Me_2SO, $Me_2N\cdot CHO$ *(DMF)) are described. Also given are reliable preparative procedures for the known* trans-$[Co(en)_2N_3X]ClO_4$ *(X = Br, Cl). The kinetics and steric course of spontaneous aquation at 25 °C have been determined for the four* trans-*azido ions: X =* Me_2SO, $k_s = (6.0 \pm 0.3)\ 10^{-3}\ s^{-1}$, *92 ± 1%* trans *product; X = DMF,* $k_s = (2.96 \pm 0.16)\ 10^{-4}\ s^{-1}$, *92 ± 2%* trans*; X = Br,* $k_s = (9.2 \pm 0.2)\ 10^{-4}\ s^{-1}$, *91 ± 1%* trans*; X = Cl,* $k_s = (2.48 \pm 0.05)\ 10^{-4}\ s^{-1}$, *91 ± 2%* trans. *The reactions are not retentive as reported previously (X = Br, Cl). A common stereochemistry (92%* trans-$[Co(en)_2N_3(OH_2)]^{2+}$*) pertains for both anionic (*Br^-, Cl^-*) and neutral (*Me_2SO*, DMF) leaving groups. The aquation mechanism is discussed.*

Introduction

The precise determination of the steric course of spontaneous aquation of several *cis*-$[Co(en)_2AX]^{n+}$ ions has revealed [1] that the *cis* isomers do not aquate with retention, as long believed. The amount of rearrangement depends upon the nature of the 'orientating' group A, and it is substantial for, *e.g.*, A = Br (38%), and N_3 (16%), Cl (25%). Moreover the stereochemical result is independent of the leaving group (Cl^-, Br^-, Me_2SO). This includes the especially good leaving groups (N_4O, HgX^+, Me_2SO_2) generated in the induced aquation reactions [1], and this result seems to dispel another long standing notion, namely that the mechanisms of spontaneous and induced aquation are fundamentally different.

A natural extension was a study of the corresponding reactions of the *trans* isomers. The ions *trans*-$[Co(en)_2N_3X]^{n+}$ (X = Br, Cl) were chosen because they have been reported to aquate with retention [2], whereas the *cis* isomers certainly aquate with rearrangement [1], and this behaviour is anomalous. Furthermore the azido systems were synthetically difficult and stereochemical studies of the aquation and base hydrolysis reactions have a history of errors [2, 3]. Clearly these aspects required attention and hence, together with the rates and revised values for the steric course of aquation, we report reliable methods for the preparation, purification and characterization of *trans*-$[Co(en)_2N_3X]^+$ (X = Cl, Br). We also report the synthesis, kinetics and steric course of aquation of the new complexes *trans*-$[Co(en)_2N_3(sol)](ClO_4)_2$ ((sol = Me_2SO, DMF)). This provides a variation in the formal charge of the leaving group, believed to be mechanistically important, and supplements a related study [4] on the putative *trans*-solvento complexes.

Experimental Section

Visible absorption spectra were measured using a Cary 118C recording instrument thermostatted to 25 °C. ^1H NMR spectra were recorded at 30 °C for Me_2SO-d_6 and D_2O (10^{-2} *M* in DCl) solutions of complex (~0.1 *M*) using a Varian T60 spectrometer and tetramethylsilane and sodium trimethylsilyl propanesulfonate as internal references respectively. The equipment and techniques for the kinetic and steric course studies (25.00 ± 0.05 °C) have been described [1, 4]. Chemicals were AnalaR grade.

Trans-$[Co(en)_2(N_3)_2]ClO_4$

This complex was prepared by a known procedure [3]. *Trans*-$[Co(en)_2(OH_2)N_3]^{2+}$ was prepared from *trans*-$[Co(en)_2(OH_2)OH](ClO_4)_2$ and aqueous NaN_3 and isolated in the form of its double salt *trans*-$[Co(en)_2(OH_2)N_3]$*trans*-$[Co(en)_2(OH)N_3](ClO_4)_3$ [1]. This was recrystallized twice as described [1] to remove traces of *trans*-$[Co(en)_2(N_3)_2]ClO_4$, and finally dried *in vacuo* over P_2O_5 (ϵ_{554}^{max} 255.5, 0.01 *M* $HClO_4$). *Cis*-$[Co(en)_2(OH_2)N_3]S_2O_6\cdot H_2O$, from *cis*-$[Co(en)_2N_3Cl]Cl$ and Hg^{2+}_{aq}, was recrystallized

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twice from water/ethanol, rather than water/methanol as given earlier [1]. This procedure reproducibly yields the alcohol free (^{1}H NMR spectrum) monohydrate on drying in air. *Anal.* Calcd. for $[Co(C_4H_{16}N_4)N_3OH_2]$ $S_2O_6 \cdot H_2O$: C, 11.51; H, 4.83; N, 23.50; S, 15.37%. Found: C, 11.70; H, 4.83; N, 23.36; S, 15.30%. Vis. spectrum: ϵ_{508}^{max} 306.2 (0.01 *M* $HClO_4$). (±) and (+)*cis*-$[Co(en)_2N_3X]ClO_4$ (X = Br, Cl) were from batches fully characterized previously [1].

Trans-*[Co(en)$_2$N$_3$Cl]ClO$_4$*

A mixture of concentrated hydrochloric acid (360 ml) and ice (120 g) was stirred until the ice had just melted (T ~ 12 °C). This was added immediately and in one lot to finely crystallized *trans*-$[Co(en)_2(N_3)_2]ClO_4$ (40 g) [FUME HOOD! Toxic HN_3 is evolved], stirred vigorously for 30 s, and then filtered to remove unreacted diazido complex. After a further 2 min, $NaClO_4$ (150 g) in cold water (300 ml) was added and the mixture quickly cooled to ~5 °C in an ice-salt bath. Blue crystals quickly appeared on scratching, and after 15 min magnetic stirring at low temperature, they were collected, washed with alcohol and ether, and dried in air. Yield: 12.0 g (The yield may be increased to ~18 g by once recycling the recovered diazido complex). The crude *trans*-$[Co(en)_2N_3Cl]ClO_4$ product was recrystallized from DMF (30 ml, ~25 °C) by the addition of a $NaHCO_3/Na_2CO_3$ buffer (0.2 *M*, 150 ml, ~15 °C) followed by, after 1 min, excess cold $HClO_4$ (30 ml 70% + 50 g ice). The quickly cooled (~5 °C) solution yielded deep blue crystals (6.0 g) which were collected after 30 min and washed and dried as above. *Anal.* Calcd. for $[Co(C_4H_{16}N_4)N_3Cl]ClO_4$: C, 13.49; H, 4.53; N, 27.54; Cl, 19.91%. Found: C, 13.59; H, 4.61; N, 27.74; Cl, 19.81%. Vis. spectra: ϵ_{579}^{max} 269.0, ϵ_{485}^{min} 35.2 (0.01 *M* $HClO_4$); ϵ_{575}^{max} 291.5, ϵ_{483}^{min} 34.0 (DMF).

Trans-*[Co(en)$_2$N$_3$Br]ClO$_4$*

The method described above was followed using diazido complex (100 g) in concentrated hydrobromic acid (600 ml) containing (melted) ice (200 g) at 12 °C. Aqueous $NaClO_4$ (150 g in 300 ml) was added after 4.0 min reaction time. Yield: 26.5 g (deep emerald green). The crude product was freed of a substantial *trans*-$[Co(en)_2Br_2]ClO_4$ impurity by two recrystallizations from DMF (5 °C) by the addition of HCO_3^-/CO_3^{2-} (pH 10) buffer (5 °C, 30 s reaction time) followed by excess cold 5 *M* $HClO_4$. Yield: 7.5 g. *Anal.* Calcd. for $[Co(C_4H_{16}N_4)N_3Br]ClO_4$: C, 11.99; H, 4.03; N, 24.48; Br, 19.95; Cl, 8.85%. Found: C, 12.05; H, 4.12; N, 24.44; Br, 19.81; Cl, 8.80%. Vis. spectra: ϵ_{594}^{max} 292.5, ϵ_{492}^{min} 26.5 (0.01 *M* $HClO_4$); ϵ_{593}^{max} 325.0, ϵ_{494}^{min} 31.5 (DMF).

Trans-[Co(en)$_2$N$_3$(DMF)](ClO$_4$)$_2$

$Hg(ClO_4)_2 \cdot 3H_2O$ (5.7 g, ~0.7 equiv.) was added in small portions (~0.5 g) to DMF (50 ml, ~5 °C) while well stirred. After complete dissolution, it was added to *trans*-$[Co(en)_2N_3Cl]ClO_4$ (6.0 g, 1.0 equiv.) in DMF (40 ml, ~20 °C). The deep blue solution quickly turned violet, and after 3 min the mixture was poured into n-butanol (300 ml). Ether (1.5 l) was added with stirring to produce a thick oil which solidified on further stirring (5 min). To the filtered solid (dissolved in water, 500 ml, ~20 °C) was added $NaClO_4$ (30 g) which quickly produced deep mauve crystals. After 15 min at ~0 °C these were collected, washed with ethanol and ether, and air dried. Yield: 6.2 g. The product was recrystallized twice from water (~350 ml, ~10 °C) by filtering to remove traces of insoluble Hg(II) residues and by the addition of saturated aqueous $NaClO_4$ (50 ml). Deep mauve needles (5.2 g) were obtained which were dried *in vacuo* over P_2O_5. *Anal.* Calcd. .for $[Co(C_4H_{16}N_4)N_3(C_3H_7NO)](ClO_4)_2$: C, 17.05; H, 4.70; N, 22.73; Cl, 14.38%. Found: C, 17.12; H, 4.83; N, 22.49, Cl, 14.40%. Vis. spectrum ϵ_{557}^{max} 277.0 (0.01 *M* $HClO_4$). ^{1}H NMR spectra: δ 7.22 (1H, CHO), 5.20 (8H, NH_2), 2.95 (3H, CH_3), 2.77 (3H, CH_3), 2.62 (8H, NCH_2); *cf.* free DMF: δ 7.78 (111, 7.78), 2.83 (3H, CH_3), 2.67 (3H, CH_3) (Me_2SO-d_6). δ 7.27 (1H, CHO), 5.17 (8H, NH_2), 3.07 (3H, CH_3), 2.87 (3H, CH_3), 2.83 (8H, NCH_2); *cf.* free DMF: δ 7.83 (1H, CHO), 2.97 (3H, CH_3), 2.78 (3H, CH_3) (10^{-3} *M* DCl).

Trans-*[Co(en)$_2$N$_3$(Me$_2$SO)](ClO$_4$)$_2$*

This complex was prepared from *trans*-$[Co(en)_2N_3Cl]ClO_4$, or better *trans*-$[Co(en)_2N_3Br]ClO_4$, by the method described above using Me_2SO (~18 °C) in place of DMF. Cold water (~5 °C) was used in all crystallizations because of its rapid rate of aquation. Deep blue violet needles (2.3 g) were obtained from the *trans*-bromoazido complex (4.0 g). *Anal.* Calcd. for $[Co(C_4H_{16}N_4)N_3(C_3H_9SO)](ClO_4)_2$: C, 14.46; H, 4.45; N, 19.69; S, 6.44; Cl, 14.23%. Found: C, 14.76; H, 4.43; N, 19.91; S, 6.49; Cl, 14.24%. Vis. spectrum: ϵ_{562}^{max} 267.6 (0.01 *M* $HClO_4$). ^{1}H NMR spectra: δ 5.20 (8H, NH_2), 2.65 (6H, CH_3), 2.63 (8H, NCH_2); *cf.* free Me_2SO, δ 2.50 (6H, CH_3) (Me_2SO-d_6). δ 5.13 (8H, NH_2), 2.87 (8H, NCH_2), 2.70 (6H, CH_3); *cf.* free Me_2SO, δ 2.63 (10^{-3} *M* DCl).

Chromatographic Experiments

Samples (~100 mg) of *cis*-$[Co(en)_2(OH_2)N_3]S_2O_6 \cdot H_2O$ and *trans*-$[Co(en)_2(OH_2)N_3]$. *trans*-$[Co(en)_2(OH)N_3](ClO_4)_3$ each eluted as a single band from Sephadex SPC25 (Na^+ form) cation exchange resin in both the acid (2+ ion; $NaClO_4$, 0.1 *M*, pH3 ($HClO_4$) eluent) and basic (+ion; Na_2HPO_4, 0.05 *M*) pH regions. In separate experiments under the latter

TABLE I. Isosbestic Points and Calculated Steric Course for the Spontaneous Aquation of *trans*-[$Co(en)_2N_3X$]$^{n+}$ in 0.01–0.1 *M* $HClO_4$ at 25 °C.

Reactant	Observed Isosbestic Points ϵ_{obs} (M^{-1} cm^{-1}), λ(nm)	Molar Absorptivities of pure [$Co(en)_2(OH_2)N_3$]$^{2+}$		% *trans* Product[a]	
		ε(*cis*)	ε(*trans*)		
trans-[$Co(en)_2N_3Br$]$^+$	232.0 (568)	128.2	239.4	93.5	92
	64.0 (453)	126.3	57.2	90	
trans-[$Co(en)_2N_3Cl$]$^+$	242.4 (562)	135.3	251.1	92.5	91
	101.8 (433.5)	132.2	98.1	89	
trans-[$Co(en)_2N_3(Me_2SO)$]$^{2+}$	250.0 (552)	175.9	255.5	93	93
	60.7 (456)	133.4	55.8	93.5	
trans-[$Co(en)_2N_3(DMF)$]$^{2+}$	210.2 (531)	250.2	205.8	90	93
	91.9 (436)	127.7	90.4	96	

[a] Calculated from the relation % *trans* = 10^2 $(\epsilon_{obs} - \epsilon_{cis})/(\epsilon_{trans} - \epsilon_{cis})$.

TABLE II. First-order Rate Constants for the Aquation of *trans*-[$Co(en)_2N_3X$]$^{n+}$ and Isomerization of [$Co(en)_2N_3(OH_2)$]$^{2+}$ in Dilute $HClO_4$ at 25 °C.[a]

Starting Complex	[$HClO_4$], *M*	10^4 k_s, s^{-1} [b]	10^4 k_s, s^{-1} [c]	10^4 k_i, s^{-1} [c]
trans-[$Co(en)_2N_3(OH_2)$]$^{2+}$	0.01			1.57 ± 0.04(2)
	0.1			1.70 ±0.05(2)
trans-[$Co(en)_2N_3Br$]$^+$	0.1	9.25 ± 0.25(3)	9.50 ± 0.50(3)[d]	1.80 ± 0.09(3)[d]
			9.4 ± 0.50(3)[e]	1.75(1)[e]
trans-[$Co(en)_2N_3Cl$]$^+$	0.1	2.48 ± 0.05(3)	2.32 ± 0.08(3)[d]	1.54 ± 0.05(3)[d]
				1.68 ± 0.03(3)[e,f]
trans-[$Co(en)_2N_3(DMF)$]$^{2+}$	0.01		2.96 ± 0.16(4)[d]	1.65 ± 0.04(4)[d]
trans-[$Co(en)_2N_3(Me_2SO)$]$^{2+}$	0.01	60.6 ± 3.3(3)	55.2 ± 3.5(3)[d]	1.58 ± 0.05(3)[d]

[a] Mean and standard deviations given; the number of determinations is indicated in parentheses. [b] Determined from 537 nm data (the *cis-/trans-* [$Co(en)_2N_3(OH_2)$]$^{2+}$ isosbestic point). [c] Both k_s and k_i obtained from an analysis for consecutive reactions (see text). [d] From 502 nm data. [e] From 602 nm data. [f] Rate plots for consecutive reactions are completely linear. 'Accidental' linearity condition holds $(\epsilon_A - \epsilon_C)/(\epsilon_B - \epsilon_C) = k_s/(k_s - k_i)$; such plots give k_i only (Ref. 5).

conditions it was shown that the *trans-* and *cis-* [$Co(en)_2(OH)N_3$]$^+$ ions separate easily (*trans* is eluted first), and under the former conditions the potential impurities [$Co(en)_2(N_3)_2$]$^+$ and [$Co(en)_2(OH_2)_2$]$^{3+}$ separate, respectively, in front of and behind [$Co(en)_2(OH_2)N_3$]$^{2+}$. *Trans*-[$Co(en)_2N_3X$](ClO_4) (X = Br, Cl) were tested for the presence of [$Co(en)_2(N_3)_2$]$^+$ and [$Co(en)_2X_2$]$^+$ by base hydrolyzing samples (~100 mg) in 0.1 *M* OH^- (2 min; 25 °C), quenching with $HClO_4$ to pH2, and chromatographing on Sephadex as above. This base hydrolysis procedure leaves any [$Co(en)_2(N_3)_2$]$^+$ untouched, and quantitatively converts [$Co(en)_2N_3X$]$^+$ to [$Co(en)_2N_3OH$]$^+$ and any [$Co(en)_2X_2$]$^+$ to [$Co(en)_2(OH)_2$]$^+$. Similar experiments were performed on *trans*-[$Co(en)_2N_3(Me_2SO)$](ClO_4)$_2$ and *trans*-[$Co(en)_2N_3(DMF)$](ClO_4)$_2$. The latter complex produces some *trans*-[$Co(en)_2N_3(HCO_2)$]$^+$ in base but not in acid, and therefore chromatography of boiled solutions in 10^{-3} *M* $HClO_4$ (5 min, > $10t_{1/2}$ for hydrolysis to [$Co(en)_2(OH_2)N_3$]$^{2+}$) was used as a criterion for the absence of any 1+ ion impurity ([$Co(en)_2(N_3)_2$]$^+$). All these chromatographic experiments are sensitive to ⩽1% impurity, largely because of the light intensity of the azido complexes which are easily observed visually on the white resin.

Kinetics

The first order rate constants (k_s) for aquation of *trans*-[$Co(en)_2N_3Br$]$^+$, [$Co(en)_2N_3Cl$]$^+$ and [$Co(en)_2N_3(Me_2SO)$]$^{2+}$ in 0.01 or 0.1 *M* $HClO_4$ at 25.00 ±

TABLE III. Equilibrium Data[a] for *cis*- $\rightleftarrows$ *trans*-$[Co(en)_2(OH_2)N_3]^{2+}$ in 0.01–0.1 *M* $HClO_4$ at 25 °C.

Reactant	ϵ_∞, M^{-1} cm^{-1} [b]							% *cis*^{502} [c]	% *cis*(ave.)[d]
	517nm (max)	446nm (min)	602nm	582nm	537[f]nm	502nm	482nm		
trans-$[Co(en)_2N_3(OH_2)]^{2+}$ (5)	248.6	103.6	81.7	126.6	230.4	234.6	180.0	67	65.5
trans-$[Co(en)_2N_3Br]^+$ (7)	251.5	108.5	86.0	131.0	232.5	239.5	184.5	69	65
trans-$[Co(en)_2N_3Cl]^+$ (4)	246.1	106.5	84.0	130.0	232.0	232.2	179.8	65.5	63.5
trans-$[Co(en)_2N_3(DMF)]^{2+}$ (2)	249.9	101.3	77.9	123.9	229.6	232.4	184.1	66	67.5
trans-$[Co(en)_2N_3(Me_2SO)]^{2+}$ (6)	250.7	101.4	78.5	124.2	232.1	237.7	184.8	68.5	68
Average	249.7	104.8	82.2	127.6	231.1	236.2	182.8	67.5 ± 1.0[e]	66 ± 1.0[e]
(+)$[Co(en)_2N_3Cl]^+$ (1)	244.5	102.4	82.4	126.1	229.0	231.1	177.8	65	64.5
(±)$[Co(en)_2N_3Cl]^+$ (1)	248.4	103.3	80.5	125.0	230.5	235.4	182.0	67	66.5
(±)$[Co(en)_2N_3Br]^+$ (1)	250.7	105.5	82.8	126.7	229.0	237.5	182.8	68.5	66
cis-$[Co(en)_2N_3(OH_2)]^{2+}$ (2)	246.6	100.7	77.7	123.0	227.5	233.1	180.0	66	67
Average	247.4	102.5	80.2	124.8	228.7	234.0	180.5	66.5 ± 1.0[e]	66 ± 1.0[e]

[a] [Co] = 2×10^{-4} to 10^{-2} *M*: the number of determinations is indicated in parentheses. [b] %cis_∞ calculated from ϵ_∞ using the relation % $cis_\infty = 10^2 (\epsilon_\infty - \epsilon_{trans})/(\epsilon_{cis} - \epsilon_{trans})$ and the following molar absorptivities for *cis*- and *trans*-$[Co(en)_2(OH_2)N_3]^{2+}$: ϵ_{cis}^{517} 294.6, ϵ_{trans}^{517} 158.8; ϵ_{cis}^{602} 56.7, ϵ_{trans}^{602} 125.8; ϵ_{cis}^{582} 88.2, ϵ_{trans}^{582} 198.0; ϵ_{cis}^{502} 303.4, ϵ_{trans}^{502} 95.8; ϵ_{cis}^{482} 242.3, ϵ_{trans}^{482} 58.2. [c] ϵ_{502} provides the most accurate result. [d] Average for five wavelengths (all except 446 and 537 nm), given equal weights. [e] Mean and standard deviation. [f] Isosbestic point between *trans*- and *cis*-$[Co(en)_2(OH_2)N_3]^{2+}$; ϵ^{537} 228.2.

0.05 °C were determined spectrophotometrically at 537 nm, the isosbestic point for the subsequent *cis*- $\rightleftarrows$ *trans*-[Co(en)$_2$N$_3$(OH$_2$)]$^{2+}$ isomerization reaction. For *trans*-[Co(en)$_2$N$_3$(DMF)]$^{2+}$ the absorbance change at 537 nm was impracticably small and both k_s and the isomerization rate constant k_i (= k_{tc} + k_{ct}) were obtained by the usual non-linear least squares analysis [1, 4] of absorbance-time data collected at 502 nm. Rate data were obtained also for the other complexes at 502 nm, as well as at 602 nm. The azido– aqua isomerization was followed at 502 nm in 0.01 and 0.1 *M* HClO$_4$ at 25 °C using the starting material *trans*-[Co(en)$_2$(OH$_2$)N$_3$], *trans*-[Co(en)$_2$(OH)N$_3$](ClO$_4$)$_3$, as earlier [1]. Equilibrium visible spectra were recorded for all reactions after 48 hr at 25 °C ($\gg 10t_{1/2}$). Light other than that from the spectrophotometer source was rigorously excluded in all experiments because of the photosensitivity of the azido complexes, particularly the aqua ions.

Results

Aqua–Azido Isomerization

We obtained the same result as previously [1] for 0.01 *M* HClO$_4$ at 25 °C, k_i = (1.57 ± 0.04) 10^{-4} s^{-1} (2). There is no significant dependence on [HClO$_4$] in the range 0.01–0.1 *M*: k_i = (1.70 ± 0.05) 10^{-4} s^{-1} (2) for 0.1 *M* HClO$_4$. The rate (Table II) and equilibrium data (Table III) differ significantly to the results of Tobe *et al.* [2] (k_i 9.6 X 10^{-5} s^{-1}, 58 ± 2% *cis* at equilibrium; 0.01 *M* HClO$_4$, 25 °C).

Aquation of trans-*[Co(en)*$_2$*N*$_3$*Br]*$^+$

Sharp isosbestic points were observed for at least one $t_{1/2}$ of aquation. The results (Table I) indicate the initial product distribution, 93 ± 2% *trans*-, 7 ± 2% cis-[Co(en)$_2$(OH$_2$)N$_3$]$^{2+}$. The rate constant for aquation k_s = (9.25 ± 0.25) X 10^{-4} s^{-1} (3) (0.1 *M* HClO$_4$, 25 °C) measured at 537 nm (Table II) is in reasonable agreement with the value of Ricevuto and Tobe [2] (8.5 X 10^{-4} s^{-1}, 0.01 *M* HClO$_4$, 25 °C), but they claim 100 ± 3% *trans* product. They obtained this result from a complete spectrophotometric analysis for the three light absorbing species present. Apart from the fact that this is not an especially accurate method, we believe the discrepancies lie in the spectra used for the *cis*- and *trans*-[Co(en)$_2$(OH$_2$)N$_3$]$^{2+}$ ions. At that time these complexes were not well characterized and the present and recent spectra [1], particularly for the *trans* ion, differ appreciably to those recorded earlier. We have confirmed our steric course result using a sensitive kinetic method described in detail elsewhere [1, 4]. The analysis for consecutive reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ using the 502 nm data yielded k_s = 9.5 X 10^{-4} s^{-1} (3), k_i = 1.8 X 10^{-4} s^{-1} (3), in good agreement with the independently measured quantities (Table II), and ϵ_B = 116.0 ± 2.5(3), which corresponds to 90.5 ± 1.5% *trans*-, 9.5 ± 1.5% *cis*-[Co(en)$_2$(OH$_2$)N$_3$]$^{2+}$ (Table IV). A very similar answer (91.5% *trans*) was obtained from the 602 nm data (Table IV), which supports the analysis.

Aquation of trans-*[Co(en)*$_2$*N*$_3$*Cl]*$^+$

The relevant results are included in Tables I–IV. The rate constant for hydrolysis k_s = (2.48 ± 0.05) 10^{-4} s^{-1} (3) agrees well with the previous value (2.6 X 10^{-4} s^{-1}, 0.01 *M* HClO$_4$, 25 °C). However we again find the 91 ± 2% *trans*-, 9 ± 2% *cis*-[Co(en)$_2$N$_3$(OH$_2$)]$^{2+}$ product distribution, in contrast to the reported retention [2]. Our results come from the usual analysis [1, 4, 5] of the plots of ln ($\epsilon - \epsilon_c$) *vs.* t which, for the 502 nm data, showed the initial

TABLE IV. Steric Course Determination for the Spontaneous Aquation of *trans*-[Co(en)$_2$N$_3$X]$^{n+}$ in 0.01–0.1 *M* HClO$_4$ at 25 °C.

Reactant	λ, nm	[HClO$_4$], *M*	10^4 k_s, k_i S^{-1} [b]	ϵ_B [a]	% trans Product[c]	
trans-[Co(en)$_2$N$_3$Br]$^+$	502	0.1	9.3, 1.70	116.0 ± 2.5(3)	90.5	91
	602	0.1	9.3, 1.70	119.9 ± 1.5(3)	91.5	
trans-[Co(en)$_2$N$_3$Cl]$^+$	502	0.1	2.48, 1.58	110.1 ± 3.0(3)	93	91 ± 2
	602	0.1	2.48, 1.58	118.2 ± 1.5(2)[d]	89	
trans-[Co(en)$_2$N$_3$(Me$_2$SO]$^{2+}$	502	0.01	60.6, 1.58	111.7 ± 1.0(3)	92.5	
trans-[Co(en)$_2$N$_3$(DMF)]$^{2+}$	502	0.01	2.96, 1.65	112.9 ± 1.5(4)	92	

[a] Calculated from ϵ, t data by a non-linear least squares analysis using the equation $\epsilon = \epsilon_c + [(\epsilon_o - \epsilon_c) + (k_s/(k_i - k_s))(\epsilon_B - \epsilon_c)] e^{-k_s t} - [(k_s/(k_i - k_s))(\epsilon_B - \epsilon_c)] e^{-k_i t}$ which applies to the consecutive first order reaction scheme $A \xrightarrow{k_s} B \xrightarrow{k_i} C$; k_s and k_i are the rate constants for spontaneous aquation and approach to equilibrium of [Co(en)$_2$(OH$_2$)N$_3$]$^{2+}$, respectively. [b] 'Best' values (see Table II). [c] Calculated from the relation % *trans* = 10^2 $(\epsilon_B - \epsilon_{cis})/(\epsilon_{trans} - \epsilon_{cis})$ using ϵ_{trans}^{502} 95.8, ϵ_{cis}^{502} 303.4 and ϵ_{trans}^{602} 125.8, ϵ_{cis} 56.7. [d] Evaluated from the extrapolated (to t = o) linear segment of the plot, which gives the intercept $(k_s/(k_s - k_i))(\epsilon_B - \epsilon_c)$ (Refs. 1, 5).

curvature followed by a later time linear section, typical of consecutive reactions. In contrast, the 602 nm data gave completely linear rate plots (k_{obs} = (1.68 ± 0.03) 10^{-4} s^{-1} (3), corresponding to k_i). This represents an interesting example of the 'accidental linearity' condition discussed in reference 5 and it arises because $(\epsilon_A - \epsilon_C)/(\epsilon_B - \epsilon_C) = k_s/(k_s - k_i)$ at this wavelength. These plots give the rate constant for the slower of the two steps, in this case k_i, and the agreement with the independently measured value is good (Table II). Moreover ϵ_B can be obtained using the linearity condition and the other measured quantities ϵ_C, k_s, k_i. The result (ϵ_B^{602} 119.9 ± 1.5) yields the calculated 91.5% *trans*, 8.5% *cis* steric course, in excellent agreement with the 502 nm (90.5% *trans*, Table IV) and isosbestic point (91% *trans*, Table I) results.

Aquation of trans-*[Co(en)$_2$N$_3$(DMF)]$^{2+}$*

Tables I–IV record the results. This new complex aquates at a rate similar to the azidochloro ion; k_s = (2.96 ± 0.16) 10^{-4} s^{-1} (4), 0.01 *M* $HClO_4$, 25 °C (Table II). The initial product distribution is 92 ± 2% *trans*-, 8 ± 2% *cis*-$[Co(en)_2N_3(OH_2)]^{2+}$ (Table IV), deduced from the analysis of the 502 nm data, and consistent with the isosbestic points (Table I).

Aquation of trans-*[Co(en)$_2$N$_3$(Me$_2$SO)]$^{2+}$*

This is the most labile of the *trans*-azido ions ($t_{1/2}$ 1.9 min, 0.01 *M* $HClO_4$, 25 °C). It reacts ~35-fold faster than the subsequent $[Co(en)_2(OH_2)N_3]^{2+}$ isomerization reaction and therefore the spectrum of the first formed product is the least affected of the four aquation reactions; accordingly the steric course determination is the most accurate. As noted elsewhere [4, 5], the term $1 - k_s/k_i$ appears in the equation used; thus the steric course calculation depends less on accrued errors in k_s and k_i the more they differ. Nonetheless the usual correction for secondary reaction was applied, and the analysis of the 502 nm absorbance-time data yielded ϵ_B = 112.9 ± 1.5(4), *i.e.*, 92 ± 1% *trans* product. For this complex, as for the relatively labile *trans*-$[Co(en)_2N_3Br]^+$ ion, both k_s and k_i could be determined separately with good precision; k_s = (6.06 ± 0.33) 10^{-3} s^{-1} [3] (3), from the 537 nm D, t data, and k_i = (1.58 ± 0.05) 10^{-4} s^{-1} (3) from the data at 502 nm following the fast initial aquation step (Table II). The latter constant agrees very closely with that measured directly (1.57 × 10^{-4} s^{-1} (2), Table II).

Equilibria

The results for the five *trans*-azido complexes are summarized in Table III. These data show that all the aquation reactions go to completion, and that at equilibrium there is 67.5 ± 1.5% *cis*- and 32.5 ± 1.5% *trans*-$[Co(en)_2(OH_2)N_3]^{2+}$ (0.01 *M* or 0.1 *M* $HClO_4$, 25 °C) irrespective of the starting material. This result is identical to that found for all the corresponding *cis*-azido complexes [1]. The molar absorbtivities of *cis*- and *trans*-$[Co(en)_2(OH_2)N_3]^{2+}$ used in the analysis are recorded in the footnote to Table III, and it is noted that the wavelengths chosen differ slightly to those used previously [1] because of slight differences between the two Cary 118C instruments employed. The present instrument was calibrated using a mercury emission spectrum, and one instrument against the other using the equilibrium spectra of (±) and (+)*cis*-$[Co(en)_2N_3X]ClO_4$ (X = Br, Cl) (Table III) measured on both spectrophotometers. The results are of course independent of the wavelengths used, but the calibration permits a direct comparison with the results recorded in Table VI of reference 1.

Discussion

Synthesis

Trans-$[Co(en)_2N_3X]ClO_4$ (X = Cl, Br) were obtained by modifications of the known method [2] in which *trans*-$[Co(en)_2(N_3)_2]^+$ is reacted with strong HX. The success of these preparations depends critically on reaction time, temperature and acid concentration since the two steps

$$\textit{trans}\text{-}[Co(en)_2(N_3)_2]^+ \rightarrow [Co(en)_2N_3X]^+ \rightarrow$$
$$\rightarrow [Co(en)_2X_2]^+$$

do not differ much in rate. Better control was achieved by using a lower temperature, lower [HX] and longer reaction times than previously. It was important to allow complete reaction of the dissolved *trans*-diazido complex since this ion is exceedingly difficult to remove from crude *trans*-$[Co(en)_2N_3X]ClO_4$ by fractional crystallization. Although this precaution lowers the yield and increases the contamination of the crude product with *trans*-$[Co(en)_2X_2]ClO_4$, the latter is easily removed through recrystallisation from a HCO_3^-/CO_3^{2-} buffer which selectively and completely base hydrolyses the dihalo complex (15 °C, $t_{1/2}$ ~ 24 min for the *trans*-chloro–azido ion). The overall yield is increased by ~50% by recycling the undissolved *trans*-$[Co(en)_2(N_3)_2]ClO_4$ complex. The starting diazido complex is obtained in >90% yield in a single step from basic starting materials [3]. This offsets the low yield for *trans*-$[Co(en)_2N_3Cl]ClO_4$ (~20%) and the bromo analog (~10%) and makes the present procedures preferable to new ones [1] described recently.

The two new *trans*-solvento complexes were obtained in good yield (~80%) by the Hg^{2+} assisted solvolysis of *trans*-$[Co(en)_2N_3X]^+$ (X = Cl or Br) in Me_2SO or DMF. The method is analogous to that described for the preparation of *trans*-[Co(en)$_2$-

(Me_2SO)Cl]$^{2+}$ from *trans*-[$Co(en)_2Cl_2$]$^+$, the first *trans*-solvento complex to be isolated [6]. In the present cases however the amount of *trans* product is much greater (80% *vs.* ~15%). We will be reporting on the stereochemistry of these reactions in detail elsewhere, but note here that the change in solvent from water to Me_2SO or DMF leads to some but not the substantial reduction in the *trans* product observed for the *trans*-dichloro complex [7].

The solvento complexes were characterized by their ^1H NMR and visible spectra which are indicative of the *trans* configuration and O-bonded solvent ligands [4]. For the known [1, 7] *cis* isomers, Me_2SO and $OCH{\cdot}N(CH_3)_2$ signals appear with different chemical shifts and the ^1H NMR spectra therefore established the isomeric purity. The *trans* isomers are less soluble than their *cis* forms and were easily freed of any *cis* by recrystallization from water as their diperchlorates. The reverse solubility order (*cis* < *trans*) is found for the nitrate perchlorate salts.

Elemental analysis does not distinguish [$Co(en)_2N_3X$]$^+$ from an ~1.1 [$Co(en)_2(N_3)_2$]$^+$ and [$Co(en)_2X_2$]$^+$ mixture. However selective base hydrolysis followed by acidification converts [$Co(en)_2N_3X$]$^{n+}$ to the 2+ ion [$Co(en)_2N_3(OH_2)$]$^{2+}$, [$Co(en)_2X_2$]$^+$ to the 3+ ion [$Co(en)_2(OH_2)_2$]$^{3+}$, while leaving the 1+ ion [$Co(en)_2(N_3)_2$]$^+$ unaffected. Therefore the stoichiometry of the four *trans*-azido–X complexes was easily established by ion-exchange chromatography of the acidified base hydrolysis products; in each case a single 2+ ion was eluted from the column.

Kinetics

The *trans*-azido–Me_2SO ion aquates very rapidly ($t_{1/2}$ ~ 1.9 min, 25 °C) and apart from the unique *trans*-sulfito complexes it is the most reactive *trans*-[$Co(en)_2AX$]$^{n+}$ ion, amongst isolated complexes, reported to date. It aquates ~25-fold faster than the *cis* form ($t_{1/2}$ ~ 48 min) [1] and this unusual difference in reactivity between isomers is attributed to the neutral leaving group and the effect has been commented on previously [4]. In contrast the azido–bromo and chloro complexes aquate at rates very similar to those for their *cis* forms, while the usual rate sequence Br > Cl (~4-fold) is observed.

Trans-[$Co(en)_2N_3(DMF)$]$^{2+}$ aquates ~20-fold more slowly than the Me_2SO complex at 25 °C. A similar although smaller rate difference (~12-fold) is observed with [$Co(NH_3)_5(sol)$]$^{3+}$ (sol = DMF, Me_2SO) [8] and it is tempting to suggest that DMF binds to Co(III) more strongly than Me_2SO. However, for *cis*-[$Co(en)_2Cl(sol)$]$^{2+}$ the rate difference involves a factor of only ~2 (although the Me_2SO complex is still faster) [9]. These results illustrate that comparisons of rate constants at a specific temperature are in general not informative unless the constants differ markedly and the activation enthalpies are similar. At least for *cis*-[$Co(en)_2Cl(sol)$]$^{2+}$ (sol = DMF, Me_2SO), the activation enthalpies are identical [9] ($\Delta H^\ddagger$, 26.6 Kcal mol^{-1}) and hence the rate difference (~X2) is the same at all temperatures*. There is no guarantee this situation pertains for the other aquation reactions. Rate comparisons between analogous Me_2SO and H_2O complexes expose a similar difficulty. For example, [$Co(NH_3)_5(Me_2SO)$]$^{3+}$ is ~3-fold more reactive [8] than [$Co(NH_3)_5OH_2$]$^{3+}$ (H_2O exchange) [10], while a similar trend appears true** for *trans*-[$Co(en)_2Cl(sol)$]$^{2+}$ (~3-fold) and *trans*-[$Co(en)_2N_3(sol)$]$^{2+}$ (~4-fold) (sol = Me_2SO, H_2O, 25 °C). In contrast, the corresponding rates for *cis*-[$Co(en)_2N_3(sol)$]$^{2+}$ appear to be reversed (H_2O ~ 2-fold faster) and the same appears to be true of *cis*-[$Co(en)_2Cl(Sol)$]$^{2+}$ (H_2O, ~5 fold faster)**. Where data are available, the activation enthalpies for the aquation of all these O-bonded neutral ligands are not significantly different, and it is abundantly clear that the relative rates do not simply reflect a single property (*e.g.*, metal–ligand bond strength). Although the effects of at least two variables (the degree of charge separation on dissociation, and anion solvation by the solvent) have been minimized by making comparisons between neutral leaving groups the relative rates still depend obviously upon the starting geometry and properties of the orientating group A in [$Co(en)_2AX$]$^{n+}$.

Steric Course of Aquation

The same stereochemical result was obtained for the four *trans*-[$Co(en)_2N_3X$]$^{n+}$ ions (X = Br$^-$, Cl$^-$, DMF, Me_2SO), 92 ± 2% *trans* product, and this result differs to that obtained [2] by Ricevuto and Tobe for the azido–bromo and –chloro complexes (100 ± 3% *trans*). At the retentive end of the steric course scale this difference of ~8% is significant with respect to product proportions. Our data indicate a *trans/cis* product ratio of *ca.* 11 whereas the previous result indicated a ratio of >30:1. Since the steric course is now defined the observation of a constant product proportion, *i.e.*, independent of leaving group, assumes importance. The leaving groups include both the anionic Br$^-$, Cl$^-$ and neutral Me_2SO, DMF and it is anticipated that a revision

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*At least in the temperature range for which $\Delta H^\ddagger$ was determined, albeit small.

**The water exchange rates are calculated from the (known) isomerization rate constants k_{ct}, k_{ct} and steric course of water substitution, assumed to be very similar for all [$Co(en)_2AX$]$^{n+}$, irrespective of X. This is generally true (see, *e.g.*, ref. 11).

of the steric course results [2, 3, 11] for the induced aquation reactions *trans*-$[Co(en)_2(N_3)_2]^+$ + NO^+ or Hg^{2+} and *trans*-$[Co(en)_2N_3X]^+$ (X = Br, Cl) + Hg^{2+} will follow the pattern 92% *trans*-, 8% *cis*-$[Co(en)_2N_3(OH_2)]^{2+}$. At the moment the *trans*-azido results are accommodated by a common pentacoordinate intermediate $[Co(en)_2N_3]^{2+}$, as seems to be the general case for the spontaneous and induced aquation of all the *cis* isomers [1] (although the common *cis* intermediate is different, and leads to 85% *cis*-, 15% *trans*-$[Co(en)_2N_3(OH_2)]^{2+}$ product [1]).

The azido systems together with $[Co(en)_2BrX]^+$ are the only ones where the *cis* isomers give more steric change in spontaneous aquation than do the *trans*. And it remains generally true, for the aquation of $[Co(en)_2AX]^{n+}$, that where the *trans* isomer rearranges so also does the *cis* form. The only exceptions appear to be $[Co(en)_2(OAc)X]^+$ [12, 13] and $[Co(en)_2(NCS)X]^+$ [14] and these systems could be revisited.

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