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Competition Studies and Stereochemistry of Base Hydrolysis of (Dimethyl sulfoxide)- and (Trimethyl phosphate)amminebis(ethylenediamine)cobalt(III) Ions

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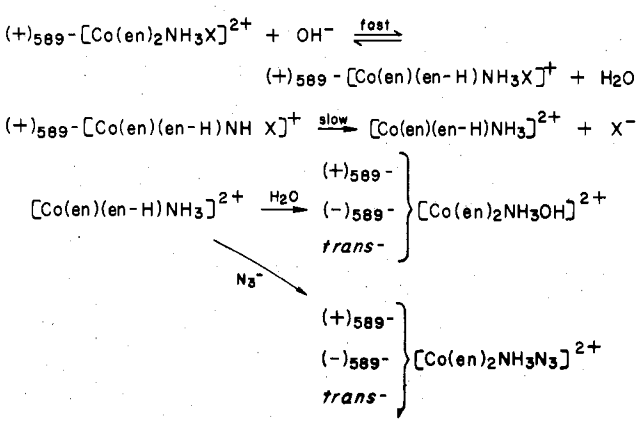
The preparation, properties, and base hydrolysis of $(+)_{589}$-$[Co(en)_2NH_3(Me_2SO)](ClO_4)_2(NO_3)$ (**1**) and $(+)_{589}$-$[Co(en)_2NH_3(TMP)](ClO_4)_3$ (**2**) (Me_2SO = dimethyl sulfoxide; TMP = trimethyl phosphate) are reported; $k_{OH}(\mathbf{1}) = 2.35 \times 10^2$ and $k_{OH}(\mathbf{2}) = 2.5 \times 10^3$ mol dm^{-3} s^{-1} in 1.0 mol dm^{-3} $NaClO_4$ at 25 °C. Base hydrolysis of **1** involves 100% Co–O bond breaking, and Cl_2 oxidation gives 100% optical retention in the $(+)_{589}$-$[Co(en)_2NH_3(OH_2)]^{3+}$ product. Base hydrolysis of $(+)_{589}$-$[Co(en)_2NH_3X]^{2+,3+}$ (X = Br, Me_2SO, TMP) gives 77% trans and 23% cis hydroxo products, but the retention in the cis ion varies with X (78% (Br^-), 83.5% (Me_2SO), 85% (TMP)); these ratios are independent of both the electrolyte (NaN_3, $NaClO_4$) and its concentration (0–2 mol dm^{-3}). The relative amounts of *cis*- and *trans*-$[Co(en)_2NH_3N_3]^{2+}$ formed in the presence of N_3^- are independent of N_3^- concentration (66% cis, 34% trans), but the retention in the cis azide also depends on X (73.5% (Br^-), 83% (Me_2SO), 85% (TMP)); marginally more (~3%) azide products are formed for X = Me_2SO and TMP than for X = Br. The results are interpreted in terms of an ion-pairing mechanism for base hydrolysis.

Recent studies on the mechanism of base hydrolysis of acidopentaamminecobalt(III) complexes support a limiting S_N1cB mechanism.[1-5] These studies embrace competition experiments[1-3] and the stereochemistry of the products,[3-5] and the conclusion concerning the mechanism was drawn from the fact that all results were independent of the nature of the leaving group. However, recent studies using three different $[Co(Metren)NH_3X]^{2+,3+}$ isomers suggest that the stereochemistry is not independent of leaving group (X = Cl^-, Br^-, NH_3),[6] and we report here some additional results on the competition products of base hydrolysis of three $(+)_{589}$-$[Co(en)_2NH_3X]^{2+,3+}$ complexes which also show a leaving group dependence.

The previous results on the base hydrolysis of the $(+)_{589}$-$[Co(en)_2NH_3X]^{2+}$ ions (X^- = Cl^-, Br^-, NO_3^-)[3] gave common stereochemistries and competition ratios for both the hydroxo and azido products (N_3^- present) with the former result agreeing with that obtained in the absence of N_3^-. This was interpreted in terms of the S_N1cB mechanism in which the five-coordinate intermediate (or intermediates) competed for various solvated leaving groups including water as depicted by Scheme I.

Scheme I



The present results extend these studies to include the neutral leaving groups Me_2SO (dimethyl sulfoxide) and TMP (trimethyl phosphate). The preparation and base hydrolysis of $(+)_{589}$-$[Co(en)_2NH_3(Me_2SO)](NO_3)(ClO_4)_2$ and $(+)_{589}$-$[Co(en)_2NH_3TMP](ClO_4)_3$ have not been reported previously, and the position of bond cleavage of the Me_2SO moiety is examined. Also, the stereochemistry of the Cl_2-induced oxidation of the Me_2SO complex is reported.

Experimental Section

$(+)_{589}$-[Co(en)$_2$NH$_3$Cl]Br$_2$ was prepared as described by Werner[7] $[\alpha]^{25}{}_{589}$ +135°. Anal. Calcd for $[CoC_4H_{16}N_4NH_3Cl]Br_2$: N, 17.89; H, 4.89; C, 12.27. Found: N, 17.8; H, 4.9; C, 12.1.

***cis*-[Co(en)$_2$NH$_3$Br]Br$_2$** was prepared from *trans*-$[Co(en)_2Br_2]Br$ as follows. *trans*-$[Co(en)_2Br_2]Br$ (48 g) was ground to a paste with 15 cm^3 of H_2O and 15 cm^3 of MeOH; a few crystals of $Co(NO_3)_2 \cdot 6H_2O$ were added, followed closely by addition of NH_4OH (sp gr 0.88 g cm^{-3}) from a Pasteur pipet. On mixture the green starting complex rapidly changed to the mauve product. Additional $MeOH-H_2O$ (80:20) was added from time to time to keep the mixture workable, and after 1 h the product was extracted with MeOH and washed on a glass filter; yield 48 g. Anal. Calcd for $[CoC_4H_{16}N_4NH_3Br]Cl_2$: N, 16.07; H, 4.39; C, 11.02. Found: N, 15.9; H, 4.5; C, 10.9. This material could be converted to the perchlorate salt by passing an aqueous solution through Dowex AG 1-X8 (ClO_4^-) exchange resin, concentration on a rotary evaporator, and addition of $NaClO_4$. Anal. Calcd for $[CoC_4H_{16}N_4NH_3Br](ClO_4)_2$: N, 14.75; H, 4.03; C, 10.11. Found: N, 14.7; H, 4.2; C, 10.1. This complex was resolved according to the method of Kauffman and Lindley.[8] The $(+)_{589}$-BCS diastereoisomer ($[\alpha]_{589}$ = +105°) was converted to the Cl^- salt by passing an aqueous solution through Dowex AG 1-X4 (Cl^-) exchange resin, concentrating it on a rotary evaporator, and adding concentrated HCl. Anal. Calcd for $[CoC_4H_{16}N_4NH_3Br]Cl_2$: N, 20.19; H, 5.52; C, 13.84. Found: N, 20.1; H, 5.4; C, 13.8. $[\alpha]^{25}$ was +125° (589 nm), −340° (436 nm), +68° (656 nm) for a 0.1% aqueous solution. For the $(-)_{589}$ salt, $[\alpha]^{25}{}_{589}$ was −125°.

$(+)_{589}$-[Co(en)$_2$NH$_3$Me$_2$SO](ClO$_4$)$_2$NO$_3$. To $(+)_{589}$-$[Co(en)_2NH_3Br]Cl_2$ (2.1 g) suspended in Me_2SO (20 cm^3) was added $AgClO_4$ (3.8 g, 3 equiv). On standing, the solution immediately

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precipitated AgCl, and after 1 h further $AgClO_4$ (1 g) was added. After 12 h AgCl was removed on a "hyflo" filter and the product reduced to a red oil by addition of EtOH and ether. Dissolution in MeOH and precipitation with *i*-PrOH produced a red product. This was crystallized from H_2O by addition of $NaNO_3$ and $NaClO_4$ and cooling of the solution in an ice bath. It was recrystallized from warm water, washed with MeOH, and air-dried. Anal. Calcd for $[CoC_4H_{16}N_4C_2H_6SO](ClO_4)_2NO_3$: N, 15.70; H, 4.71; C, 13.46. Found: C, 15.6; H, 5.2; C, 13.6. ϵ_{max} at 505 nm was 85.2 and at 351 nm was 87.2. $[\alpha]^{25}{}_{589}$ was found to be +132°.

The ^{18}O-labeled *cis*-$[Co(en)_2NH_3Me_2S^{18}O](ClO_4)_2NO_3$ (ca. 1.3 g) was similarly made by using ^{18}O-enriched Me_2SO (1.2 atom %).

$(+)_{589}$-$[Co(en)_2NH_3(CH_3O)_3PO](ClO_4)_3$. To $(+)_{589}$-$[Co(en)_2NH_3Br]Cl_2$ (2.2 g) in dry trimethyl phosphate (20 cm^3, 4A molecular sieve) was added $AgClO_4$ (4 g). AgCl precipitated immediately, and after 1 h further $AgClO_4$ (1 g) was added. After standing for 2 days in the dark, the solution was filtered on a "hyflo" filter; *i*-PrOH (50 cm^3) was added to the filtrate followed by excess dry ether. The resulting red gum was washed with Et_2O and redissolved in MeOH; the solution was filtered, and *i*-PrOH was added followed by ether. This dry residue was dissolved in dry MeOH (20 cm^3) and induced to crystallize by scratching. The red-orange powder was washed with a little dry MeOH and ether and air-dried. Anal. Calcd for $[CoC_4H_{16}N_4NH_3C_3H_9PO_4](ClO_4)_3$: N, 11.04; H, 4.45; C, 13.25. Found: N, 11.0; H, 4.5; C, 13.1. ϵ_{max} at 500 nm was 69 and at 347 nm was 60. $[\alpha]^{25}{}_{589}$ was found to be +92° and $[\alpha]^{25}{}_{436}$ was −152°.

^{18}O-Labeled Me_2SO. This was prepared from Me_2S via the dibromo addition compound following the method of Fries and Vogt.[9] Me_2S (30 g) was added to dry *n*-hexane (250 cm^3) in a 1 dm^3 round-bottomed flask cooled to −5 °C. Br_2 (30 g) in *n*-hexane (50 cm^3) was slowly added over 45 min such that the temperature was maintained below 0 °C. The yellow slurry of Me_2SBr_2 was allowed to settle and hexane decanted off. $H_2{}^{18}O$ (20 cm^3, 1.5 atom %) was then added with good stirring giving a pale yellow oil. Further hexane was added (100 cm^3), followed by NaOH pellets (40 g) over 30 min with good stirring (*care*). The neutralized solution was then allowed to warm to room temperature and additional NaOH added until the water layer became solid. The *n*-hexane was removed by rotary evaporation and the Me_2SO distilled into a liquid nitrogen trap by warming to 40 °C under reduced pressure. The crude product was twice fractionated at 3 mmHg, and the product boiled at 53–55 °C; yield 7.5 g. Mass spectrum (MS 902 spectrometer): for product, 100[80]/([78] + [80]) = 5.6%; for Me_2SO (unenriched), 4.4%; enrichment in $^{18}O \simeq 1.2\%$.

$(+)_{589}$-$[Co(en)_2NH_3H_2O]Br_3 \cdot H_2O$, $(+)_{589}$-$[Co(en)_2NH_3N_3]Cl_2$, *trans*-$[Co(en)_2NH_3H_2O](NO_3)_3$, and *trans*-$[Co(en)_2NH_3N_3]S_2O_6$ were as prepared previously.[3] Data (used in evaluating the products of hydrolysis) were as follows. $(+)_{589}$-$[Co(en)_2NH_3H_2O]Br_3 \cdot H_2O$: ϵ(484 nm) 68.7 mol^{-1} dm^3 cm^{-1}, $[M]_{589}$ +370°, $[M]_{436}$ −1010°. *trans*-$[Co(en)_2NH_3H_2O]^{3+}$: ϵ(485 nm) 45.5 mol^{-1} dm^3 cm^{-1}, both in 1.0 mol dm^{-3} HCl. $(+)_{589}$-$[Co(en)_2NH_3N_3]Cl_2$: ϵ(508 nm) 347 mol^{-1} dm^3 cm^{-1}, $[M]_{480}$ −2180°. *trans*-$[Co(en)_2NH_3N_3]S_2O_6$: ϵ(512 nm) 277 mol^{-1} dm^3 cm^{-1}, both in 1.0 mol dm^{-3} $NaClO_4$.

Base Hydrolysis Rates. These were followed by pH stat titration against 0.05 mol dm^{-3} NaOH with a Radiometer ABU 12 Autoburette in conjunction with a PHM 62 pH meter, REA Titrograph, and TTT 60 titrator. About 10^{-4} mol of complex in 40 cm^3 of 1.0 mol dm^{-3} $NaClO_4$ was used for each run. $[OH]^-$ was calculated by using $pK_w = 13.77$.[10]

Competition Experiments. The competition experiments were carried out in groups of three, one of each complex ($X = Br^-$, Me_2SO, TMP) per group. Approximately 60–70 mg of complex was dissolved either in 5 cm^3 of 2.0 or 1.0 mol dm^{-3} $NaClO_4$, in 0.5 mol dm^{-3} NaN_3/0.5 mol dm^{-3} $NaClO_4$, or in 1.0 and 2.0 mol dm^{-3} NaN_3, each adjusted to pH ~7 at 25.0 °C. A solution of NaOH (5 mL, 0.4 mol dm^{-3}) containing the salt mixture was rapidly added at 25.0 °C and the mixture left for 3 min. The solutions were then neutralized by addition of 2 cm^3 of 1.0 mol dm^{-3} $HClO_4$, dilution to 500–800 cm^3, and adsorption onto an ion-exchange column (Sephadex SP-25, Na^+ form, 12 × 1 cm). The column was washed with H_2O, and the $[Co(en)_2NH_3N_3]^{2+}$ ions were eluted with 0.2 mol dm^{-3} $NaClO_4$. These were readsorbed directly onto a larger (30 × 1 cm) column of Dowex 50W-X2 resin (Na^+ form, packed in 0.2 mol dm^{-3} $NaClO_4$), and the cis and trans isomers separated and eluted with 1.0 mol dm^{-3} $NaClO_4$. The orange aqua ions remaining on the Sephadex column were eluted with 1.0 mol dm^{-3} HCl. In each case, eluate volumes were measured (the aqua species were usually made up to 50 cm^3 in standard flasks with HCl) and visible spectra immediately recorded (Cary 118C spectrophotometer). Co concentrations were determined by atomic absorption measurements (Techtron Model AA-4) and optical rotations measured on a Perkin-Elmer P22 Spectropolarimeter. Each set of experiments was repeated at least five times, and recovery of the complexes from the ion-exchange column was quantitative (100 ± 1%).

Hg^{2+}-Induced Aquation of $(+)_{589}$-$[Co(en)_2NH_3Br]Cl_2$ and Cl_2 Oxidation of $(+)_{589}$-$[Co(en)_2NH_3Me_2SO](ClO_4)_2(NO_3)$. The complex (0.02–0.03 g) was dissolved in water (5 cm^3) and 5 cm^3 of 2.0 mol dm^{-3} $NaClO_4$ added. A solution of $Hg(ClO_4)_2$ (10 cm^3, 0.5 mol dm^{-3} Hg^{2+} in 1.0 mol dm^{-3} $HClO_4$) was added to the bromo complex at 25.0 °C, and Cl_2 was bubbled through the solution of the Me_2SO complex at ~5 °C. Reaction times were 20 and 3 min, respectively. Following dilution (200 cm^3) the complexes were adsorbed on ion-exchange columns (Dowex 50W-X2, 12 × 1 cm) and eluted with NaCl solution (1.0 mol dm^{-3}, Hg^{2+} experiment) and then with 2.0 mol dm^{-3} HCl. For the Cl_2 oxidation, ~5% of the $[Co(en)_2NH_3Cl]^{2+}$ was recovered. The aqua products were collected and visible spectra, rotations, and concentrations (atomic absorption) measured. The experiments were run in duplicate.

^{18}O-Labeling Experiment: Base Hydrolysis of *cis*-$[Co(en)_2NH_3Me_2S^{18}O](ClO_4)_2NO_3$. *cis*-$[Co(en)_2NH_3Me_2S^{18}O](ClO_4)_2NO_3$ (1.0 g) in water (20 cm^3) was base hydrolyzed by pH stat titration at pH 10.0 (6 min, 25.0 °C); the solution was reduced to near dryness on a rotary evaporator and concentrated HBr (10 cm^3) added. The red-orange product was triturated with ethanol at ~0 °C, and the $[Co(en)_2NH_3H_2O]Br_3 \cdot H_2O$ was collected and washed with ethanol and ether and dried in air (yield 0.8 g). The visible spectrum in 1.0 mol dm^{-3} HCl gave ϵ(484 nm) 68.7 mol^{-1} dm^3 cm^{-1}. This material was dried overnight at 30 °C and 10^{-3} mmHg in a Urey tube to remove the H_2O of crystallization, and the temperature was then raised to 100 °C for 15 h to remove the coordinated water. After freezing (liquid N_2) and pumping to remove extraneous gases, we distilled the water into a break-seal tube containing $HgCl_2$ and $Hg(CN)_2$ (0.2 g). Heating at 400 °C for 6 h converted the water to CO_2 which was collected and analyzed by comparison with a standard CO_2 sample as described previously[11] (Atlas Mat GD-150 mass spectrometer): $R_{obsd} = [46]/[44] + [46], =0.00320$; $R_{blank} = 0.00341$.

To obtain the ^{18}O enrichment in the *cis*-$[Co(en)_2NH_3Me_2SO](ClO_4)_2NO_3$, we converted a sample (0.3 g) to the bromide salt (AG 1-X4 resin, Br^- form), and after rotary evaporation to dryness, residual water was removed by heating overnight at 80 °C and 10^{-4} mmHg. This material was then decomposed with the $HgCl_2/Hg(CN)_2$ mixture as described above, and the CO_2 was collected and analyzed as previously: $R_{obsd} = 0.02284$; $R_{blank} = 0.00335$. Atom percent enrichment = $(100R/2 + R) - (100R_{blank}/2 + R_{blank}) = 0.96\%$.

Results

$[Co(en)_2NH_3Me_2SO](ClO_4)_2NO_3$ and $[Co(en)_2NH_3TMP](ClO_4)_3$ were prepared from $[Co(en)_2NH_3Br]Br_2$ by using $AgClO_4$ to remove bromide in dry dimethyl sulfoxide and trimethyl phosphate. Optically pure $(+)_{589}$-$[Co(en)_2NH_3Me_2SO](ClO_4)_2NO_3$ and $(+)_{589}$-$[Co(en)_2NH_3TMP](ClO_4)_3$ were similarly prepared from $(+)_{589}$-$[Co(en)_2NH_3Br]Cl_2$. The optical purity of the former was confirmed by treatment with Cl_2 from which largely $(+)_{589}$-$[Co(en)_2NH_3H_2O]^{3+}$ was produced ($[M]_{589}$ +370°; $[M]_{420}$ −1100°) together with some 8% $(+)_{589}$-$[Co(en)_2NH_3Cl]^{2+}$. This is consistent with the previous results using $[Co(NH_3)_5Me_2SO](ClO_4)_3$.[12] These data not only confirm the full retention of configuration in the Cl_2 oxidation experiment[13] but also show that a similar result holds for the Ag^+-induced removal of Br^-. Neither result was unexpected.

Base hydrolysis of $[Co(en)_2NH_3Me_2SO](ClO_4)_2NO_3$ and $[Co(en)_2NH_3TMP](ClO_4)_3$ follows the normal pattern found with other acidopentaaminecobalt(III) complexes although few 3+ reactant complexes have been examined so far.[14] Rate data given in Table I clearly follow the rate law $k_{obsd} = k_{OH}[OH^-]$ at least up to ~10^{-4} mol dm^{-3} OH^-. The second-order rate constants ($k_{OH} = 2.35 \times 10^2$ mol^{-1} dm^3 s^{-1} (Me_2SO) and 2.5 × 10^3 mol^{-1} dm^3 s^{-1} (TMP)) are larger than that for [Co-

Table I. Base Hydrolysis Rate Data for *cis*-$[Co(en)_2NH_3Me_2SO](ClO_4)_2NO_3$ and *cis*-$[Co(en)_2NH_3TMP](ClO_4)_3$[b]

pH	10^3k_{obsd}, s^{-1}	$10^6[OH^-]$, mol dm^{-3}	$10^{-2}k_{OH}$,[a] mol^{-1} dm^3 s^{-1}
cis-$[Co(en)_2NH_3Me_2SO](ClO_4)_2NO_3$			
8.30	0.85	3.39	2.51
8.50	1.33	5.37	2.48
8.70	2.05	8.51	2.41
8.91	3.41	13.8	2.47
9.12	4.81	22.4	2.15
9.33	7.80	36.3	2.15
9.53	13.9	57.5	2.42
9.74	20.8	93.3	2.23
cis-$[Co(en)_2NH_3TMP](ClO_4)_3$			
7.00	0.46	0.17	26.9
7.20	0.73	0.27	27.1
7.40	1.10	0.43	25.6
7.60	1.71	0.68	25.3
7.80	2.49	1.07	23.3
8.00	4.01	1.70	23.6
8.20	6.52	2.69	24.2

[a] $k_{OH} = k_{obsd}/[OH^-]$. [b] At 25 °C in 1.0 mol dm^{-3} $NaClO_4$.

Table II. Stereochemistry of the Products Formed in the Base Hydrolysis of $(+)_{589}$-$[Co(en)_2NH_3X]^{2+,3+}$ Ions[a]

X	$[NaClO_4]$, mol dm^{-3}	% $[Co(en)_2NH_3OH]^{2+}$		
		trans	ΔΛ-cis	Λ-cis
Br^-	0.0	22.0	34.2	43.8
	1.0	22.0	34.0	44.0
	2.0	22.2	33.8	44.0
Me_2SO	0.0	23.1	25.6	51.3
	1.0	22.9	25.4	51.7
	2.0	23.3	25.1	51.6
TMP	0.0	22.5	24.0	53.5
	1.0	22.5	23.2	54.3
	2.0	22.7	23.2	54.1

[a] In the presence of $NaClO_4$ at 25.0 °C.

$(en)_2NH_3Br]^{2+}$ (k_{OH} = 35 mol^{-1} dm^3 s^{-1}) in 1.0 mol dm^{-3} $NaClO_4$,[15] and Me_2SO and TMP can be labeled as "good" leaving groups.

The position of bond cleavage was examined by using the $Me_2S^{18}O$-labeled complex. Base hydrolysis at pH 10 and recovery of the $[Co(en)_2NH_3H_2O]Br_3$ showed no enrichment in the coordinated water. This is to be compared with an enrichment of 0.96 atom % in the initial complex. Thus base hydrolysis involves quantitative Co–O bond cleavage. The similar experiment with the TMP complex was not done, and from the previous results of Schmidt and Taube[16] some CoO–$P(OMe)_3$ bond fission might have been expected (they found ~12% with $[Co(NH_3)_5TMP]^{3+}$). However the products of hydrolysis (see below) compare closely with those for $[Co(en)_2NH_3Me_2SO]^{3+}$, and the rate is particularly fast, so we expect complete Co–O cleavage for this complex as well. Certainly no CoO–P bond cleavage occurs in the very much slower hydrolysis of the acetyl phosphate complex $[(NH_3)_5CoOPO_3COCH_3]^+$[17] and the previous result for $[(NH_3)_5CoTMP]^{3+}$[16] bears repeating.

Products of Base Hydrolysis. The products resulting from the base hydrolysis of the $[Co(en)_2NH_3X]^{2+,3+}$ ions (X = Br^-, Me_2SO, TMP) in the presence of 0.0–2.0 mol dm^{-3} $NaClO_4$ are given in Table II. Results in the presence of added N_3^- are given in Table III. Each experiment was carried out five times with the four closest results being averaged and the fifth discarded. The maximum deviation of any one result from the average was 1.5% ($(+)_{589}$), 0.4% ($(-)_{589}$), and 0.6% (trans) for the hydroxo products and 0.7% ($(+)_{589}$), 0.4% ($(-)_{589}$), and –0.5% (trans) for the azido products; the estimated error in each result is better than ±0.5%. Within this uncertainty the results show: (1) no effect on varying the ionic strength from 0.0 to 2.0 mol dm^{-3} $NaClO_4$, Table II; (2) a constant cis:trans ratio independent of leaving group X and of the presence or absence of N_3^- (these results hold for both the CoOH and CoN_3 products, Tables I and II); (3) a stereochemical retention in the cis CoOH and cis CoN_3 products which depends on X, showing significantly more retention for the 3+ reactants than for X = Br^- (this stereochemical retention appears to be independent of the N_3^- concentration, Tables II and III); (4) a competition ratio $R = 100[CoN_3]/[CoOH][N_3^-]$ which decreases slightly with increasing $[N_3^-]$, Table IV; (5) a competition for N_3^- which is slightly larger for the Me_2SO and TMP complexes (3+ ions) than it is for X^- = Br^-, Table IV.

Table III. Competition Values and Stereochemistry of the Products Formed in the Base Hydrolysis of $(+)_{589}$-$[Co(en)_2NH_3X]^{2+,3+}$ Ions[a]

X	$[NaN_3]$ and $[NaClO_4]$, mol dm^{-3}		$[Co(en)_2NH_3OH]^{2+}$			$[Co(en)_2NH_3N_3]^{2+}$		
			trans	ΔΛ-cis	Λ-cis	trans	ΔΛ-cis	Λ-cis
Br^-	0.5	0.5	18.6	27.7	36.7	5.7	6.1	5.2
	1.0	0.0	15.7	25.4	31.6	7.9	10.3	9.1
	2.0	0.0	13.0	19.3	25.8	14.1	14.2	13.6
Me_2SO	0.5	0.5	16.8	21.6	42.7	6.4	4.2	8.3
	1.0	0.0	16.0	18.0	36.2	9.6	6.9	13.3
	2.0	0.0	12.3	13.9	29.6	16.3	9.5	18.4
TMP	0.5	0.5	18.2	19.4	43.0	6.6	3.8	9.0
	1.0	0.0	15.5	16.0	37.4	10.5	6.2	14.4
	2.0	0.0	12.2	12.8	29.9	15.0	8.4	21.7

[a] In the presence of NaN_3 at 25.0 °C.

Hydrolysis of the reactant complexes followed by addition of N_3^- failed to give any CoN_3 products; this is in agreement with previous observations.[3] The azido complexes are therefore formed in the base hydrolysis process. Also, addition of 0.2 mol dm^{-3} NaOH to *cis*- and *trans*-$[Co(en)_2NH_3N_3]^{2+}$ failed to give any CoOH products in the time of hydrolysis, and both the $(+)_{589}$ cis and trans CoOH ions were stable under the conditions. These observations require the analytical result to give a quantitative record of the products of hydrolysis.

From Table II it is clear that the same result is obtained independent of $NaClO_4$ concentration. Thus the presence of other ions or ionic strength effects do not influence the product composition at least for the *cis*- and *trans*-$[Co(en)_2NH_3OH]^{2+}$ species. These results agree with those obtained previously with X^- = Cl^- and NO_3^- (22, 23% trans; 30, 30% ΔΛ-cis; 48, 47% Λ-cis),[3] and a single experiment under our conditions gave 22.6% trans, 33.0% ΔΛ-cis, and 44.4% Λ-cis for $(+)_{589}$-$[Co(en)_2NH_3Cl]Br_2$. The amounts of cis and trans CoOH (77 ± 1%, 23 ± 1%) are the same for the three leaving groups, but the retention in the cis CoOH ion increases from 78% ($100\Lambda/(\Delta + \Lambda)$) for X^- = Br^- to 83.5 and 85% for X = Me_2SO and TMP. The same result holds for the CoOH products obtained in the presence of N_3^-, Table III. The cis and trans amounts remain constant at 77 and 23% for all three complexes independent of N_3^- concentration, and the retention in the cis CoOH ions (78% (Br^-), 83.5% (Me_2SO), 85% (TMP)) is also independent of N_3^- and is the same as that found in its absence. Thus the presence of N_3^- does not affect the *stereochemistry* or the *relative* amounts of the CoOH products, but the leaving group X does, diverting some racemic ΔΛ-CoOH to Λ-CoOH when the anions Cl^-, Br^-, or NO_3^- are replaced by the uncharged Me_2SO or TMP ligands.

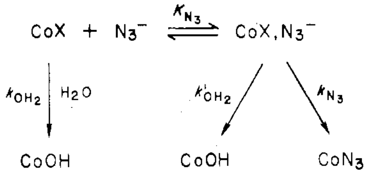
Similar conclusions can be made from the CoN_3 results. The amounts of cis and trans CoN_3 are maintained at 66 ± 1% and 34 ± 1% for each of the leaving groups independent of N_3^- concentration, but the retention in the *cis*-CoN_3 species

Table IV. Competition Ratios at Different Azide Concentrations (25.0 °C)

$[N_3^-]$, mol dm^{-3}	R values (trans, Δ, Λ), %[a]		
	X = Br	X = Me_2SO	X = TMP
0.5 (+0.5 (ClO_4^-))	41 (61, 44, 33)	47 (76, 39, 46)	48 (73, 39, 39)
1.0	37.5 (50, 41, 32)	42 (53, 40, 39)	45 (68, 39, 39)
2.0	36 (54, 37, 29)	40 (66, 34, 32)	41 (61, 33, 37)

[a] $R = 100[Co-N_3]_T/[Co-OH]_T[N_3^-]$, where $[Co-N_3]_T$ and $[Co-OH]_T$ represent the total (cis + trans) products. The *R* values for the individual trans, Δ (inversion), and Λ (retention) ions are given in that order in parentheses.

Scheme II



is substantially greater for the 3+ reactants (100Λ/(Δ + Λ) = 73.5% (Br), 83% (Me_2SO), 85% (TMP)). It may be significant that for the more symmetrical 3+ ions the retentions in the cis CoN_3 and cis CoOH products agree.

Table IV gives competition ratios expressed as

$$R = 100[CoN_3]_T/[CoOH]_T[N_3^-]$$

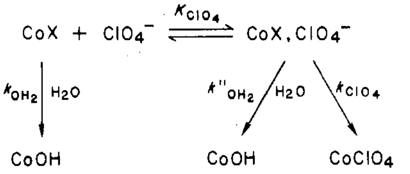
where $[CoN_3]_T$ and $[CoOH]_T$ represent the total (T) cis + trans amounts. The decreasing values for all three complexes with increasing N_3^- concentration require the contribution of a pathway to CoOH which is N_3^- dependent as well as the normal independent one (see below). Also, although the data is limited, the $[N_3^-]$-dependent pathway appears to be more significant for the more highly charged Me_2SO and TMP complexes (larger change in *R*), and N_3^- competition is larger overall (larger *R*). Both factors support entry from an ion-paired substrate $[Co(en)_2NH_3X]^{2+,3+},N_3^-$ for part of the process at least. Similar trends in *R* for the individual Λ, Δ, and trans species obtain (values are given in parentheses in Table IV) so that these effects are felt in each of the products. Also, the individual *R* values show a decided preference for trans entry of N_3^- compared to trans entry of water when comparison is made with the cis products (larger *R* value), and for the bromo complex N_3^- entry appears to give more of the inverted Δ product than water entry when comparison is made with the stereochemical retentive paths. For the 3+ complexes the *R* values for the Λ and Δ products agree within the accuracy of the results.

Discussion

The varying stereochemistries observed in the CoN_3 and CoOH products from the base hydrolysis of $(+)_{589}$-*cis*-$[Co(en)_2NH_3X]^{2+,3+}$ ions (X = Cl^-, Br^-, NO_3^-, Me_2SO, TMP) cannot be rationalized in terms of a limiting S_N1cB mechanism. Such a process requires a common intermediate, or set of intermediates, for the different substrates, Scheme I.[3,18] Previous data have shown that the Cl^-, Br^-, and NO_3^- results agree,[3] but the new results for the Me_2SO and TMP complexes give substantially more retention in the cis CoOH and cis CoN_3 products than that observed with the other leaving groups. The results are independent of the ionic environment (0.0–2.0 mol dm^{-3} $NaClO_4$ or NaN_3) so that medium effects are not responsible. Clearly a leaving group dependence as distinct from a medium or ion-pairing effect is involved.

The results can be accommodated by Scheme II. CoX represents $(+)_{589}$-*cis*-$[Co(en)_2NH_3X]^{2+,3+}$, and CoOH and CoN_3 represent the various *trans*-, Δ-*cis*-, and Λ-*cis*-$[Co(en)_2NH_3OH]^{2+}$ and -$[Co(en)_2NH_3N_3]^{2+}$ products. There is good evidence to suggest that under the conditions (pH ≤12) the CoOH product is derived from H_2O entry rather than OH^- entry. Green and Taube[19] demonstrated this for base hydrolysis of $[Co(NH_3)_5X]^{2+}$ ($X^- = Cl^-, Br^-, NO_3^-$) by using the large isotopic fractionation between $^{16}OH^-$ and $^{18}OH^-$, and other studies have shown product compositions in the presence of anionic competitors which are OH^- independent.[2,20] A path involving OH^- entry does however appear to become important above 0.1 mol dm^{-3} OH^-.[21] The above scheme leads to a product ratio (eq 1), which agrees with the observed data

Scheme III



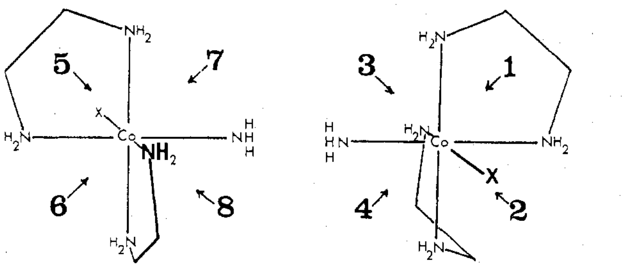
$$R = \frac{[CoN_3]_T}{[CoOH]_T[N_3^-]} = \frac{k_{N_3}K_{N_3}}{k_{OH_2} + k'_{OH_2}K_{N_3}[N_3^-]} \quad (1)$$

(Table IV). The k'_{OH_2} term for entry of H_2O from the ion pair makes a small but clearly apparent contribution to the CoOH product and is the azide-dependent contribution mentioned in the Results section.

Allowance can be made for a similar ClO_4^- ion pair, and under the conditions this could lead to CoOH and $CoClO_4$ products (Scheme III). However the independence of the CoOH stereochemistry in the presence or absence of $NaClO_4$ (and NaN_3) requires the k''_{OH_2} (and k'_{OH_2}) path to give the same products as the k_{OH_2} path. Also, entry of ClO_4^- to give $CoClO_4$ must be unimportant since some *trans*-$[Co(en)_2NH_3ClO_4]^{2+}$ would be expected, and the subsequent rapid hydrolysis of this species would increase the trans and ΔΛ-cis CoOH content. Thus *trans*-$[Co(en)_2NH_3X]^{2+}$ ($X^- = Cl^-, NO_3^-$) gives some 36% *trans*- and 64% ΔΛ-*cis*-$[Co(en)_2NH_3OH]^{2+,3+}$. Obviously the observed stereochemistry is independent of ClO_4^- concentration (Table II), and this supports the view that ClO_4^- is a poor entering group (compared to N_3^-). Furthermore, another study on the base hydrolysis of $[Co(tren)(NH_3)_2]^{3+}$ gives an ion-pair constant for OH^- (K_{OH}) of ~3.0 relative to ClO_4^- (this is distinguished from a deprotonation constant),[22] and if a similar value obtains for N_3^- with the present 3+ ions, the results (Table IV) would require k'_{OH_2} to contribute only 1–5% toward the CoOH products. Therefore, even if the k'_{OH_2} path did give a different stereochemical result, its contribution would not be large. The ionic strength independence shown in the CoOH products therefore probably arises from the k_{OH_2} path, i.e., from the non-azide ion-paired species.

The slightly larger *R* value for the 3+ Me_2SO and TMP complexes and the somewhat smaller change in *R* for the 2+ bromo complex are both consistent with a larger ion-pair constant, K_{N_3}, for the 3+ substrates. This has also been observed in the base hydrolysis of $[Co(NH_3)_5Me_2SO]^{3+}$ in the presence of N_3^- where an *R* value of 14% has been found, compared to 10% for the 2+ ions ($X^- = Cl^-, Br^-, NO_3^-, CF_3SO_3^-$).[23]

So far we have not considered the question of intermediates of reduced coordination number and whether H_2O and N_3^- enter from such species. Clearly the leaving group X could still exert an influence even if the Co–X bond was completely broken but X was still present adjacent to the five-coordinate intermediate. Provided the k'_{OH_2} (and k''_{OH_2}) term does not contribute meaningfully to the CoOH products, the present results do not contribute to this question. If it is significant, then the constant stereochemistry independent of the presence or absence of ion pairs places severe restrictions on the



(a)	Backside Attack		
5	trans (en)	Δ (en)	
6	trans (en)		
7		Δ (en)	Λ (NH_3)
8			Λ (NH_3)

(b)	Frontside Attack			
1				Λ (O)
2	trans (en)?			Λ (O)
3		Λ (en)?	Λ (en)?	Λ (O)
4			Λ (NH_3)?	Λ (O)

Figure 1. (a) Backside (5–8) and (b) frontside (1–4) entry of incoming groups on the octahedral faces of Λ-$(+)_{589}$-*cis*-$Co(en)_2NH_3X^{2+,3+}$. The groups undergoing movement are indicated in brackets.

properties of such five-coordinate intermediates. They would be required to give different stereochemical products arising from the adjacent but now detached X group such that the Δ-cis:Λ-cis ratio changed with the X group but the total cis product remained constant. This would be required for intermediates giving both CoOH and CoN_3 products. This is at variance with the properties of the N_3^- or ClO_4^- ion pairs which give the same stereochemical result (in CoOH) as that from the non-ion-paired intermediates. Thus X and N_3^- (or ClO_4^-) exert different influences, and for $X^- = Br^-$ at least (and also for $X^- = Cl^-$, NO_3^-, etc.) this is difficult to imagine unless X remains at least partly bound to the metal.[25] There is other evidence to suggest that if a five-coordinate intermediate has any existence at all, it is insufficient to allow for the adjustment of bond angles about the metal or for rearrangement of the ionic solvation sheath.[6] This limits the lifetime to about 10^{-11}–10^{-14} s, appreciably shorter than that required for diffusion into or out of the solvation shell from the bulk medium. Such intermediates must inherit the environment of the reactant ion and essentially scavenge (rather than compete) for immediately available, and probably correctly oriented, entering groups. This lifetime must approach that required to completely sever the Co–X bond, and in this case no intermediate would occur at all. We prefer to picture the mechanism as an I_d process, with X remaining "partly" bonded to cobalt as H_2O or the anionic competitor becomes associated with the metal.

It remains to discuss the product stereochemistries and the conjugate base part of the mechanism. The results of Green and Taube[19] imply that the OH^- ion used in proton abstraction is not involved as an entering group. The critical position of deprotonation which leads to hydrolysis remains unclear at the present time but could be adjacent to (frontside)[18] or removed from (backside)[3] the octahedral faces containing X. However the NMR relaxation results of Grunwald and Wong with the Pt(IV) conjugate base $[Pt(NH_3)_5NH_2]^{3+}$[24] imply that the deprotonation site will be very rapidly equilibrated between all available amine centers in the $[Co(en)(en\text{-}H)NH_3X]^{+,2+}$ species and that this process is much faster than diffusion from the bulk solvent. Thus even if the site of proton abstraction is not that required for hydrolysis, it will rapidly become so (in an equilibrium sense), and the solvation sheath containing N_3^- (ClO_4^-) as well as H_2O molecules will remain trapped in its initial substrate configuration. It is not possible at this time to positively identify the directions of entry of H_2O or N_3^-, but the present results provide some clues. Both frontside and backside entry are possible, and our analysis is contained in Figure 1. The frontside view (Figure 1(b)) shows that entry from each of the four octahedral faces leads largely, if not entirely, to retention of the Λ-cis configuration. Faces 2 and 3 could possibly give some trans and Δ-cis product, respectively, but this would involve movement of an ethylenediamine amine group or NH_3 about a common octahedral edge and toward the incoming H_2O or N_3^- group. Direct substitution for X seems much more likely. Backside entry (Figure 1(a)) appears to be the only method for forming trans and inverted Δ-cis products, and faces 5 and 7 allow two possible stereochemical results from the one face. Provided each position of entry acts independently, as the above discussion suggests, the X-dependent Δ-cis:Λ-cis ratio arises naturally from competitive movement of NH_3 and ethylenediamine amine groups away from substitution at face 7. Faces 6 and 5 lead to only trans and retentive Λ-cis products, respectively. Face 5 could form either trans or Δ-cis products, but in view of the X-independent trans:Δ-cis results (for both CoOH and CoN_3) H_2O or N_3^- entry from this site is less likely. To include it would require one wing of the ethylenediamine moiety to move at the exclusion of the other or that the ratio is X independent for this part. In view of the X-dependent result for face 7, the latter possibility seems unlikely. In summary, the products most naturally arise from entry (and consequently ion-pair formation with N_3^-) from positions adjacent to X (front side) and from faces 6, 7, and 8 distant from X. The larger proportions of trans and Δ-cis products for N_3^- is in agreement with a greater amount of backside entry for the anionic species.

Registry No. **1**, 69991-13-5; **2**, 69991-15-7; *trans*-$[Co(en)_2NH_3OH]^{2+}$, 38246-62-7; Δ-(−)-*cis*-$[Co(en)_2NH_3OH]^{2+}$, 18660-71-4; Λ-(+)-*cis*-$[Co(en)_2NH_3OH]^{2+}$, 45837-83-0; *trans*-$[Co(en)_2NH_3N_3]^{2+}$, 46139-36-0; Δ-(−)-*cis*-$[Co(en)_2NH_3N_3]^{2+}$, 39502-32-4; Λ-(+)-*cis*-$[Co(en)_2NH_3N_3]^{2+}$, 46139-34-8; Λ-(−)-*cis*-$[Co(en)_2NH_3Br]Cl_2$, 60103-80-2; *cis*-$[Co(en)_2NH_3Br]Br_2$, 15306-93-1; *cis*-$[Co(en)_2NH_3Br](ClO_4)_2$, 62301-87-5; *trans*-$[Co(en)_2Br_2]Br$, 15005-14-8; Λ-(+)-*cis*-$[Co(en)_2NH_3OH_2]^{2+}$, 45837-82-9.

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