rameters for the reaction of the more rapidly reacting isomer and seem to suggest that the first reaction may involve a change from one isomer to the other in the transition state. From the limited data for this reaction, determination of the exact nature of the reaction is not feasible, although the straight-line plots seem to indicate a parallel, rather than a series, first-order reaction.

A comparison of the rate of acid hydrolysis of $Co(tren)H_2OCl^{2+}$ with that of the corresponding ethylenediamine complex shows that, at 25.0°, the tren complex reacts about 75% faster.[5] On the other hand, the acid hydrolysis of $Co(tren)Cl_2^+$ proceeds at a rate nearly 1200% larger than that of *cis*-$Co(en)_2Cl_2^+$ under similar conditions.[6]

These results are in good agreement with those already discussed in the study of the bromoaquo system and support the hypothesis that the labilization of the second halide group in dihalo(triaminotriethylamine)cobalt(III) complexes is considerably less than that of the first. The observation that the first bromo group appears to be more labilized by the distortion of the complex than the first chloro group may account for the presence of only one isomer in the bromoaquo system.

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A Stereochemical and Aquation Study of Phosphatoamminebis(ethylenediamine)cobalt(III)

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The preparations, pmr spectra, visible absorption spectra, and acid dissociation constants of *cis*-$Co(en)_2NH_3PO_4 \cdot 3H_2O$ and *trans*-$Co(en)_2NH_3PO_4 \cdot 5H_2O$ are reported. The aquations of the triprotonated species, *cis*- and *trans*-$Co(en)_2NH_3PO_4H_3^{3+}$, proceed with cobalt–oxygen bond fission and with full retention of configuration. The aquation rate parameters are $k(70°) = 17.0 \times 10^{-5}\ sec^{-1}$, $\Delta H^{\ddagger} = 27.1 \pm 0.8$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -2.8 \pm 2.4$ cal deg^{-1} mol^{-1} for *cis*-$Co(en)_2NH_3PO_4H_3^{3+}$ and $k(70°) = 16.5 \times 10^{-5}\ sec^{-1}$, $\Delta H^{\ddagger} = 27.0 \pm 0.3$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -2.6 \pm 0.8$ cal deg^{-1} mol^{-1} for *trans*-$Co(en)_2NH_3PO_4H_3^{3+}$ in 3.698 *M* perchloric acid.

Introduction

A number of phosphatoamminecobalt(III) complexes, in which phosphate functions as a monodentate ligand, have been reported, and their aquation has been studied.[2–5] Where the possibility of geometric isomerism arose, only cis isomers were detected,[4] and stereochemical aquation studies of these species were precluded by the relatively rapid isomerization rates of the possible aquo products.

The object of this study was to prepare *cis*- and *trans*-phosphatoamminebis(ethylenediamine)cobalt(III) and to investigate the stereochemical pathways of their aquations. Comparison with the sterochemical aquation characteristics reported.[6,7] for other $Co(en)_2XY$ complexes should provide further insight into the phosphato aquation mechanism.

Experimental Section

Materials.—*cis*-$[Co(en)_2NH_3H_2O]Br_3 \cdot H_2O$ and *trans*-$[Co(en)_2NH_3H_2O](NO_3)_3$ were prepared as described in the literature.[8] Other chemicals were either analytical grade or recrystallized reagent grade. Carrier-free phosphorus-32-labeled orthophosphate in dilute hydrochloric acid was obtained from AAEC, Lucas Heights, N.S.W., Australia.

cis-**Phosphatoamminebis(ethylenediamine)cobalt(III).**—A solution of 40 g of *cis*-$[Co(en)_2NH_3H_2O]Br_3 \cdot H_2O$, 120 g of $NaH_2PO_4 \cdot 2H_2O$, and 32 ml of concentrated H_3PO_4 in 200 ml of water was heated at 70° for 1 hr. This solution was then cooled to 25° and the cationic species were adsorbed onto a ~40 cm × 8 cm diameter column of Zeokarb 225 cation-exchange resin in the acid form. The column was washed with 3 l. of water and the phosphato complex was then eluted from it with 0.1 *M* NaOH at 25°. The most concentrated fraction of the effluent (*ca.* 4 l.) was cooled to 5° and was added slowly with stirring to 8 l. of acetone at 5°. After 24 hr in a refrigerator the pink flocculent precipitate was filtered off, washed with acetone, and air dried. This product was recrystallized by dissolution in the minimum amount of water at 50°, cooling to 0°, and reprecipitating by dropwise addition of concentrated NH_4OH solution. The resultant amorphous precipitate was filtered off, washed with ethanol, and air dried; yield 6 g (20.5%). *Anal.* Calcd for *cis*-$Co(en)_2NH_2PO_4 \cdot 3H_2O$: Co, 17.08; C, 13.92; N, 20.28; P, 8.97. Found: Co, 16.87; C, 14.01; N, 20.10; P, 8.90.

When *cis*-$[Co(en)_2NH_3Br]Br_2 \cdot H_2O$ was used as the starting complex, a similar yield of *cis*-$Co(en)_2NH_3PO_4 \cdot 3H_2O$ was obtained.

trans-**Phosphatoamminebis(ethylenediamine)cobalt(III).**—A solution of 34 g of $NaH_2PO_4 \cdot 2H_2O$, 75 ml of concentrated H_3PO_4, and 10 ml of water was heated to 70°. Solid *trans*-$[Co(en)_2NH_3H_2O](NO_3)_3$ (12 g) was added slowly with stirring and the resultant solution was maintained at 70° for 1 hr. This solution was then cooled to 25° and diluted with 200 ml of water, and the cationic species were adsorbed onto a ~20 cm × 8 cm diameter column of Zeokarb 225 in the acid form. The phosphato complex was eluted from the column and precipitated from solution in the same manner as the cis isomer. The precipitate was recrystallized by dissolution in the minimum amount of water at 50° and reprecipitating by cooling in a refrigerator overnight. The deep red crystals were washed with a small

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[1] To whom correspondence may be addressed.

[2] W. Schmidt and H. Taube, *Inorg. Chem.*, **2**, 698 (1963).

[3] S. F. Lincoln, J. Jayne, and J. P. Hunt, *ibid.*, **8**, 2267 (1969).

[4] S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, **21**, 37 (1968).

[5] S. F. Lincoln and D. R. Stranks, *ibid.*, **21**, 67 (1968).

[6] M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).

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[8] M. L. Tobe and D. F. Martin, *Inorg. Syn.*, **8**, 199 (1966).

amount of cold water and air dried; yield 4.5 g (14.5%). *Anal.* Calcd for *trans*-$Co(en)_2NH_3PO_4 \cdot 5H_2O$: Co, 15.46; C, 12.60; N, 18.37; P, 8.13. Found: Co, 15.15; C, 12.93; N, 18.67, P, 8.40.

Phosphorus-32-labeled *cis*- and *trans*-$Co(en)_2NH_3PO_4$ were prepared in small-scale preparations spiked with radioactive orthophosphate. Purity was checked by comparison of molar extinction coefficients with those listed in Table II.

***trans*-Aquoamminebis(ethylenediamine)cobalt(III) Perchlorate.**—A solution of 5 g of *trans*-$[Co(en)_2NH_3H_2O](NO_3)_3$ in 60 ml of water was prepared at 25°, and an equal volume of concentrated perchloric acid was added dropwise such that the temperature did not rise above 30°. This solution was left in a refrigerator overnight and the resultant orange crystals were filtered off and air dried. The crystals were just covered with water and ground into a paste at 25°. After 2 hr in a refrigerator the crystals were filtered off and air dried; yield 3 g. *Anal.* Calcd for *trans*-$[Co(en)_2NH_3H_2O](ClO_4)_3$: C, 9.43; N, 13.75. Found: C, 9.66; N, 13.57.

The extinction coefficients of the product were within 1% of those reported for the nitrate salt.[9]

Analyses.—Cobalt was determined by electrodeposition.[10] All other analyses were performed by the Australian Microanalytical Service, Melbourne, Victoria.

Proton Magnetic Resonance.—Pmr spectra were run at probe temperature (*ca.* 29°) on saturated solutions of the complex in trifluoroacetic acid, with a Varian DP-60-IL spectrometer. Glass capillaries containing TMS were placed in the pmr tubes to provide a lock signal.

Spectrophotometric Measurements.—Visible absorption spectra were run in 1-cm quartz cells with a Unicam SP700 spectrophotometer at 25° against solvent blanks. Solution concentrations were within the range $(3\text{–}12) \times 10^{-3}$ *M*.

Acid Dissociation Constants.—Solutions of the phosphato complexes (0.05 *M* in complex with ionic strength made up to unity with sodium perchlorate such that $\mu = 1$ at the half-neutralization point of the acid dissociation under investigation) were titrated against 1.000 *M* perchloric acid at 25° under carbon dioxide free nitrogen, using a Radiometer 25 pH meter. The pK_a values were calculated *via* standard methods.

Bond Fission.—Oxygen-18 tracer experiments on the aquation of *cis*- and *trans*-$Co(en)_2NH_3PO_4$ were carried out in 1.425 *M* perchloric acid prepared by the dilution of analytical grade perchloric acid with ^{18}O-enriched water (1.57 at. %, Yeda Research and Development Co., Israel) such that the ^{18}O at. % of the solvent water was 1.49. The complexes were aquated for 4 aquation half-times, and the free phosphate was separated by the ion-exchange technique used for the $^{32}PO_4^{3-}$ assay below. The phosphate in the eluent was precipitated at ice temperature as barium phosphate by the addition of ammoniacal barium nitrate. Oxygen-18 analysis was previously described.[4] Analysis of phosphate, released during aquation, for ^{18}O mass spectrographically gave 0.205 ± 0.005 and 0.204 ± 0.008 at. % ^{18}O in duplicated experiments for the phosphate released from the cis and trans isomers, respectively. The normal ^{18}O isotopic abundance is 0.204 ± 0.002%. From these data it is apparent that the aquation of $Co(en)_2NH_3PO_4H_3^{3+}$ proceeds predominantly with cobalt–oxygen bond fission. Oxygen exchange between phosphate and water in the aquation experiments above proceeds at a rate negligible by comparison to the rate of aquation.[11] A Hitachi Perkin-Elmer RMU-6D mass spectrometer was used.

Radiochemical Rate Measurements.—The techniques and data treatment employed in determining the rates of aquation of the ^{32}P-labeled complexes were as previously described.[5]

Spectrophotometric Rate Measurements.—A 50- or 100-ml aliquot of the required perchloric acid was pipetted into a stoppered reaction vessel at 25° and was heated to 70° in a water bath. An open-ended glass vessel containing preweighed complex was dropped into the reaction vessel, which was vigorously agitated to ensure rapid and complete mixing. Samples were taken over 2–2.5 isomerization or aquation half-times, and infinite-time samples were taken after 8–10 half-times for isomerization runs and, in the case of the aquation runs, after 25 isomerization half-times for the *trans*-aquo species. All samples were quenched in stoppered ice-cooled test tubes. Upon completion of a run the samples were warmed to 25° and the spectrum of each was recorded ($(15\text{–}30) \times 10^3$ cm^{-1}).

The isomerization rate constants k_{isom} for *trans*-$Co(en)_2NH_3H_2O^{3+}$ were calculated from the time dependence of optical density at 20,000 and 21,000 cm^{-1}. Good first-order rate plots were obtained by standard methods. In 4.734 *M* perchloric acid there was evidence for the formation of some nitrato complex at equilibrium, and in 9.840 *M* perchloric acid this was a predominant reaction when the nitrate salt was used. When the perchlorate salt was used, the only species detected at equilibrium was *cis*-$Co(en)_2NH_3H_2O^{3+}$.

The dissolution of the perchlorate salt was slow in 9.840 *M* perchloric acid, and the first samples taken 13 min after initiation of the runs had absorption spectra identical with that of the cis isomer indicating that isomerization was completed within this time.

The aquation of *trans*-$Co(en)_2NH_3PO_4H_3^{3+}$ was followed at the *trans*-phosphato–*trans*-aquo isosbestic point at 20,800 cm^{-1}, ϵ 45.7, in 1.058, 3.698, and 4.734 *M* perchloric acid and at the *trans*-phosphato–*cis*-aquo isosbestic point (19,900, 19,800, 19,800 cm^{-1} with ϵ 56.1, 55.2, 55.2 in 1.058, 3.698, 4.734 *M* perchloric acid, respectively). From the measured optical densities the concentration–time dependences of the *trans*-phosphato, *trans*-aquo, and *cis*-aquo species were determined.

The aquation of *cis*-$Co(en)_2NH_3PO_4H_3^{3+}$ was followed at the *cis*-phosphato–*cis*-aquo isosbestic point at 22,050 cm^{-1} where ϵ was 45.4 in 1.058, 3.698, and 4.734 *M* perchloric acid and at 19,800 cm^{-1} where *cis*-phosphato ϵ was 83.5 in 1.058 *M* perchloric acid and 81.8 in 3.698 and 4.734 *M* perchloric acid and *cis*-aquo ϵ was 55.2 in all cases. No optical density–time dependence was observed at the isosbestic point and first-order rate constants identical with those predicted *via* interpolation of the radiochemical aquation data were obtained from the optical density–time dependence at 19,800 cm^{-1}.

Results and Discussion

Proton Magnetic Resonance Spectra.—The *cis*- and *trans*-$Co(en)_2NH_3PO_4$ isomers were identified *via* their pmr and visible absorption spectra. The pmr spectra of *cis*- and *trans*-$Co(en)_2NH_3PO_4$ are shown in Figure 1.

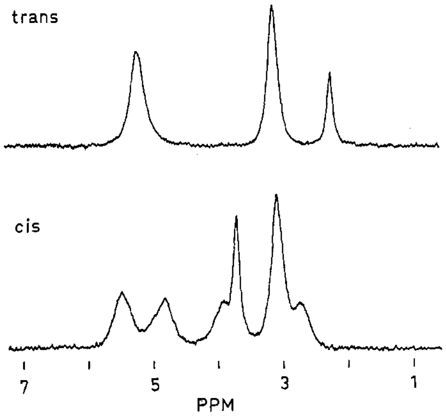

Figure 1.—Pmr spectra of *cis*- and *trans*-$Co(en)_2NH_3PO_4$ in trifluoroacetic acid.

The peak assignments for the *trans* isomer are NH_2 (5.25), NH_3 (2.28), and CH_2 (3.17), and for the cis isomer they are NH_2 (5.50, 4.82, 3.93), NH_3 (3.70), and CH_2 (3.07, 2.72), where the figures in parentheses are shifts in ppm downfield from external TMS. The peak assignments were made on the basis of integrated areas and the nonappearance of certain peaks in the spectra of the deuterated complexes.[12]

Visible Absorption Spectra.—The visible spectra of *trans*-$Co(en)_2NH_3PO_4$ and its protonated analogs are

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[9] M. L. Tobe, *J. Chem. Soc.*, 3776 (1959).

[10] A. I. Vogel, "Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1961, p 614.

[11] C. A. Bunton, D. R. Llewellyn, C. A. Vernon, and V. A. Welch, *J. Chem. Soc.*, 3293 (1960).

[12] NH protons were exchanged for deuterons by dissolution of the complexes in D_2O followed by evaporation to dryness under vacuum at 25°.

TABLE I

MOLAR EXTINCTION COEFFICIENTS FOR *cis*- AND *trans*-$\text{Co(en)}_2\text{NH}_3\text{PO}_4\text{H}_n{}^{n+}$ (25°)

Complex (R = $\text{Co(en)}_2\text{NH}_3$)	Cis isomer				Trans isomer			
	Band IA		Band II		Band IA		Band II	
	$\epsilon_{\max}$	ν, cm^{-1}	$\epsilon_{\max}$	ν, cm^{-1}	$\epsilon_{\max}$	ν, cm^{-1}	$\epsilon_{\max}$	ν, cm^{-1}
RPO_4[a]	112.5	19,500	96.2	27,600	90.5	19,200	76.5	28,000
RPO_4H^+[b]	101.5	19,600	86.4	28,000	74.9	19,400	66.7	28,300
$\text{RPO}_4\text{H}_2{}^{2+}$[c]	89.8	19,700	76.9	28,200	60.8	19,550	55.6	28,400
$\text{RPO}_4\text{H}_3{}^{3+}$[d]	81.7	19,700	69.0	28,200	56.2	19,500	52.1	28,500
$\text{RPO}_4\text{H}_4{}^{4+}$[e]	73.6	19,700	62.5	28,300	50.2	19,400	46.9	28,600

[a] Solvent 0.01 M NaOH; μ adjusted to unity with NaClO_4. [b] Solvent 0.1 M phosphate buffer (pH 6.03); μ adjusted to unity with NaClO_4. [c] Solvent 0.05 M HClO_4; μ adjusted to unity with NaClO_4. [d] Solvent 3.54 M HClO_4. [e] Solvent 11.85 M HClO_4.

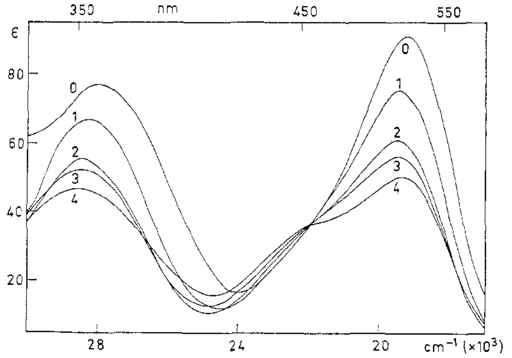

Figure 2.—Visible absorption spectra of *trans*-$\text{Co(en)}_2\text{NH}_3\text{PO}_4\text{H}_n{}^{n+}$. The number on each spectrum is equal to n in the formula of the complex to which the spectrum refers. The solvents are those listed in Table II.

shown in Figure 2, and molar extinction coefficients, ϵ, for the cis and trans isomers are listed in Table I, in which bands are labeled IA and II in order of increasing energy after the notation of Linhard and Weigel.[13,14] The spectra of the trans isomer are characterized by a shoulder which exhibits increased resolution from band IA ($^1\text{A}_{1g} \rightarrow {}^1\text{E}_g{}^a$)[15] as protonation of the phosphato ligand increases and which may be assigned as band IB ($^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$). No splitting of band II ($^1\text{A}_{1g} \rightarrow {}^1\text{B}_{2g}$ and $^1\text{A}_{1g} \rightarrow {}^1\text{E}_g{}^b$) is observed. In the spectra of the cis isomer band IB is not resolved from band IA. For both isomers, ϵ values of bands IA and II decrease with increase in protonation and in every case the cis isomer exhibits the greater ϵ value at band maxima.

The pK_a values determined titrimetrically at unit ionic strength (NaClO_4) and 25° for $\text{Co(en)}_2\text{NH}_3\text{PO}_4\text{H}^+$ (pK_{a1}) are 7.73 ± 0.05 (trans) and 7.85 ± 0.05 (cis), and for $\text{Co(en)}_2\text{NH}_3\text{PO}_4\text{H}_2{}^{2+}$ (pK_{a2}) they are 3.00 ± 0.05 (trans) and 3.20 ± 0.05 (cis). The species $\text{Co(en)}_2\text{NH}_3\text{PO}_4\text{H}_3{}^{3+}$ is postulated on the basis that there is little change in the spectra of the cis and trans isomers within the perchloric acid concentration range 2.5–6 M. This is consistent with spectral data for other phosphato systems (pK_{a3} for $\text{Co(NH}_3)_5\text{PO}_4\text{H}_3{}^{3+}$ is −0.23 determined from spectrophotometric measurements[4]) and with the interpretation of aquation rate data, as in the postulation of the species $\text{Co(en)}_2\text{NH}_3\text{PO}_4\text{H}_4{}^{4+}$ to explain the spectra observed in concentrated perchloric acid.

Kinetics of Aquation.—The radiochemically determined aquation rate constants, k_{obsd}, are listed in Table II. To facilitate discussion the rate profiles for the cis and trans species are each separated into regions I, II, III, and IV which refer to the perchloric acid concentration ranges 1.23×10^{-3}–0.123 M; 0.123–3.698 M; 3.698–7.010 M; and >7.010 M, respectively. In region I the major aquating species is $\text{Co(en)}_2\text{NH}_3\text{PO}_4\text{H}_2{}^{2+}$. The cis isomer aquates *ca.* 1.5 times more rapidly than the trans isomer within this region. The increase in k_{obsd} as perchloric acid concentration increases may be attributed to the increasing contribution of the more reactive $\text{Co(en)}_2\text{NH}_3\text{PO}_4\text{H}_3{}^{3+}$ species. No supporting electrolyte was present in the aquation studies and hence the aquation data and the pK_a data are not strictly comparable. An exhaustive investigation[3] of this region in the $\text{Co(NH}_3)_5\text{PO}_4$ system led to an identical interpretation in terms of protonated species to that given above however. In region II the tripotonated species makes an increasing contribution to the aquation rate until a maximum k_{obsd} value is observed at the high acid concentration extreme of this region.

In region III the small decrease in k_{obsd} may be attributed to a rate law of the form

$$k_{\text{obsd}}[\text{Co(en)}_2\text{NH}_3\text{PO}_4\text{H}_3{}^{3+}] = k_3[\text{Co(en)}_2\text{NH}_3\text{PO}_4\text{H}_3{}^{3+}]a_{\text{w}}$$

where k_3 is the specific first-order rate constant for the triprotonated species and a_{w} is the activity of water. This expression predicts the constancy of $k_{\text{obsd}}a_{\text{w}}{}^{-1}$ in region III which is not observed as seen in Table II. Nevertheless $k_{\text{obsd}}a_{\text{w}}{}^{-1}$ does remain constant over relatively wide perchloric acid concentration ranges in rate profiles of related phosphatoamminecobalt(III) systems,[5] and consequently it is postulated that the increasing contribution of the more reactive species $\text{Co(en)}_2\text{NH}_3\text{PO}_4\text{H}_4{}^{4+}$ to k_{obsd} obscures such an observation in the systems under investigation in this work.[16] The tetraprotonated species is considered kinetically to dominate region IV.

Activation parameters for $\text{Co(en)}_2\text{NH}_3\text{PO}_4\text{H}_3{}^{3+}$, calculated from data obtained in 3.698 M HClO_4, are $\Delta H^{\ddagger} = 27.1 \pm 0.8$ and 27.0 ± 0.3 kcal mol^{-1} and $\Delta S^{\ddagger} = -2.8 \pm 2.4$ and -2.6 ± 0.8 cal deg^{-1} mol^{-1} for the cis and trans isomers, respectively.

Stereochemistry of Aquation.—The observed first-order rate constants, k_{isom}, for the isomerization of *trans*-$\text{Co(en)}_2\text{NH}_3\text{H}_2\text{O}^{3+}$ to the cis isomer are listed in Table III. At equilibrium only the cis isomer was detected in solution. The considerable increase in k_{isom} as the acid concentration was increased is similar to that observed for the $\text{Co(en)}_2(\text{H}_2\text{O})_2{}^{3+}$ system[17] for which it was suggested that an isomerization proceeding *via* an acid-catalyzed opening of an ethylenediamine ring might assume increasing importance at higher

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(13) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **264**, 321 (1951).

(14) M. Linhard and M. Weigel, *ibid.*, **267**, 113 (1951).

(15) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

(16) It is of interest to note that the aquation of $\text{Cr(H}_2\text{O)}_5\text{OOCCH}_3$ also exhibits a rate dependence upon a_{w}: E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

(17) W. Kruse and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1280 (1961).

TABLE II
KINETIC DATA FOR THE AQUATION OF $Co(en)_2NH_3PO_4$[a]

	10^5k_{obsd}, sec^{-1}		
$[HClO_4]$, M	Cis isomer	Trans isomer	Temp, °C ($\pm0.05°$)
1.23×10^{-3}	2.10	1.56	70.0
6.16×10^{-3}	2.34	1.80	70.0
1.23×10^{-2}	2.54	1.89	70.0
6.16×10^{-2}	2.73	2.27	70.0
1.23×10^{-1}	3.46	...	70.0
6.16×10^{-1}	8.10	6.70	70.0
1.058	11.5	9.95	70.0
1.230	13.2	10.8	70.0
1.849	15.4	...	70.0
1.964	...	14.6	70.0
2.465	16.6 (18.9_3)	15.4 (17.5_6)	70.0
3.081	17.0 (20.6_1)	16.0 (19.3_9)	70.0
3.698	17.0 (22.2_0)	16.5 (21.5_7)	70.0
3.698	...	16.4 (21.4_4)	70.0
4.310	...	16.0 (23.0_2)	70.0
4.314	16.5 (23.7_4)	...	70.0
4.734	16.0 (24.9_2)	15.5 (24.1_4)	70.0
4.930	15.6 (25.3_2)	15.2 (24.6_7)	70.0
5.546	15.0 (28.4_6)	...	70.0
5.904	...	14.6 (30.4_2)	70.0
6.160	13.9 (31.3_8)	...	70.0
6.779	14.6 (41.7_1)	...	70.0
7.010	...	14.6 (45.7_7)	70.0
7.390	15.8 (59.6_2)	...	70.0
8.010	17.4 (90.1_6)	17.0 (88.0_8)	70.0
8.630	20.8	...	70.0
8.856	...	22.0	70.0
9.840	34.0	32.0	70.0
10.09	...	46.0	70.0
11.09	85.4	...	70.0
3.698	54.2	51.7	80.0
3.698	54.6	51.3	80.0
3.698	5.06	4.60	60.0
3.698	4.94	4.50	60.0
3.698	...	1.70	51.7
3.698	...	1.70	51.7
3.698	1.38	...	50.0
3.698	1.40	...	50.0

[a] Figures in parentheses in columns 2 and 3 are $k_{obsd}a_w^{-1}$. a_w data were from J. F. Bunnett, *J. Amer. Chem. Soc.*, **83,** 4966 (1961). The complex concentration in each run was within the range $(5–10) \times 10^{-5}$ M.

TABLE III
KINETIC DATA FOR THE ISOMERIZATION OF
trans-$Co(en)_2NH_3H_2O^{3+}$ AT 70.0°

10^5k_{isom}, sec^{-1}	$[HClO_4]$, M	10^5k_{isom}, sec^{-1}	$[HClO_4]$, M
3.0[a]	1.058	12.0[b]	3.544
2.9[b]	1.058	20.0[a]	4.734
12.0[a]	3.544	a, c	9.840

[a] Perchlorate salt. [b] Nitrate salt. [c] Isomerization complete in ~10 min; see Experimental Section.

acid concentrations. Such a mechanism also provides a plausible explanation of the data in Table III.

A comparison of the data in Tables II and III indicated the feasibility of stereochemical path aquation studies of $Co(en)_2PO_4H_3^{3+}$ within the perchloric acid concentration range 1.058–4.734 M. Spectrophotometric aquation runs were accordingly carried out in 1.058, 3.698, and 4.734 M perchloric acid, and both isomers were found to aquate with retention of configuration. A plot of data from a typical run is seen in Figure 3.

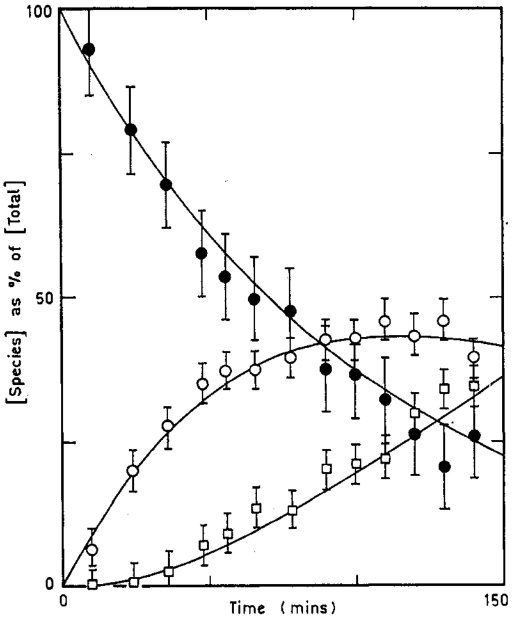

Figure 3.—Complex concentration–time dependence for the aquation of *trans*-$Co(en)_2NH_3PO_4H_3^{3+}$ in 3.698 M perchloric acid at 70°. Concentrations are expressed as a percentage of the total cobalt concentration; *trans*-$Co(en)_2NH_3PO_4H_3^{3+}$, *trans*-$Co(en)_2NH_3H_2O^{3+}$, and *cis*-$Co(en)_2NH_3H_2O^{3+}$ percentages are represented by filled circles, open circles, and open squares, respectively. The solid lines were calculated for the consecutive reactions

$$trans\text{-phosphato} \xrightarrow{k} trans\text{-aquo} \xrightarrow{k_{isom}} cis\text{-aquo}$$

where $k = 16.5 \times 10^{-5}$ sec^{-1} and $k_{isom} = 11.5 \times 10^{-5}$ sec^{-1}.

The Mechanisms of Aquation.—The close similarity in aquation rate profiles and in activation parameters of *cis*- and *trans*-$Co(en)_2NH_3PO_4H_3^{3+}$ suggests that both isomers aquate *via* similar mechanisms. The retention of configuration characterizing the aquation of these complexes is also a characteristic of the other complexes of the $Co(en)_2NH_3X$ type all of which are considered to aquate *via* a dissociative mechanism probably with solvent assistance.[6,7] On this basis it seems likely that the phosphato complexes also aquate *via* such a mechanism.

The apparent aquation rate dependence on a_w is consistent with both associative and dissociative mechanisms under certain conditions.[3,5] Hence a mechanistic differentiation on this basis does not seem possible, especially as the nature of the second coordination sphere may change significantly with variation in a_w.

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