time up to 25 min at 0°. The spectrum remains identical with that of *trans*-Co(en)$_2$(H$_2$O)$_2^{3+}$ and is quite different from that of the *trans*-Co(en)$_2$H$_2$OCl^{2+} cation. Under these reaction conditions the proposed anation of the *trans*-dihydroxo complex to the *trans*-chlorohydroxo intermediate should have been complete in a few seconds and the chlorohydroxo intermediate should have been 80–90% converted to the *cis*-dihydroxo complex in this time. However, in order to induce any change in the spectrum within a reasonable time, it was necessary to raise the temperature. At 50.8°, samples withdrawn from time to time, cooled, and acidified gave a set of spectra with isosbestic points at 551, 446, 385, and 348 mμ which were fully consistent with those of mixtures of *cis*- and *trans*-Co(en)$_2$(H$_2$O)$_2^{3+}$[4] and were essentially identical with spectra obtained under the same conditions but in the absence of chloride. The spectrophotometric change followed a first-order rate law and the rate constant was independent of the wavelength and independent of the concentration of hydroxide and chloride. The value obtained, 4.4×10^{-4} sec^{-1}, is identical with that reported in the absence of chloride.[4-7]

The second test of the Dittmar–Archer mechanism arises from the reversibility of the fast stereoretentive base hydrolysis. This would require that the *trans*-Co(en)$_2$OHCl$^+$ cation exchanges its chloride rapidly with free chloride ions in solution. We therefore took a solution of [*trans*-Co(en)$_2$OHCl]Cl in alkali, under similar conditions to those reported by Dittmar and Archer, except for the presence of Na^{36}Cl, and, after stopping the reaction at various stages, isolated the unreacted complex as [*trans*-Co(en)$_2$H$_2$OCl][B(C$_6$H$_5$)$_4$]$_2$. The data reported in Table I indicate that, even after there has been considerable base hydrolysis, there is no significant exchange of the chloride in the unreacted complex.

TABLE I

UPTAKE OF ^{36}Cl IN UNREACTED *trans*-Co(en)$_2$OHCl$^+$ AT 0°[a]

Time, sec	% reaction	$10^{-2} \times$ specific activity of [*trans*-Co(en)$_2$H$_2$OCl][B(C$_6$H$_5$)$_4$]$_2$, counts/mmol min	% exchange
40	13	7.8	0.26
60	18	6.9	0.23
90	29	9.5	0.32
180	38	10.9	0.36

[a] Initial [complex] = 0.050 *M*; [NaCl] = 0.04 *M*; initial [OH$^-$] = 0.16 *M*; specific activity of Cl^{*-} = 1.08×10^6 counts/mmol min.

Thus we have been unable to find any evidence that supports the mechanism of Dittmar and Archer and can only assume that their observation of the rapid formation of *trans*-Co(en)$_2$(OH)$_2^+$ is the consequence of the overrefinement of their data by means of a computer. Therefore, there is no reason to change significantly the original data for the rates and steric course of the base hydrolysis of *trans*-Co(en)$_2$OHCl$^+$.[2]

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The *cis–trans* Equilibrium of Diaquobis(ethylenediamine)cobalt(III) Ion in Nitrate and Perchlorate Media

By ROBERT C. HENNEY

Since the diaquobis(ethylenediamine)cobalt(III) ion is the product in acid hydrolysis of the acido-substituted parent compounds, the *cis–trans* and acid–base equilibria of the system are important in kinetic and mechanistic studies of aquation. Bjerrum and Rasmussen,[1] in a careful study of the system in 1 *M* sodium nitrate, reported the *cis:trans* equilibrium ratio to be 58, a figure subsequently used by other investigators working in different ionic media.[2-5] Investigation in this laboratory confirmed the findings of Bjerrum and Rasmussen; however, pmr spectra[6] suggested a greater amount of *trans* ion in perchlorate medium. The validity of comparing studies in the two media had already been questioned;[7] accordingly a determination of the effects of the two ions on the *cis:trans* equilibrium ratio was undertaken.

Experimental Section

The *cis:trans* ratios of diaquobis(ethylenediamine)cobalt(III) ion in perchlorate and nitrate media were determined by potentiometry, by spectrophotometry, and by pmr measurements.

Preparation of Compounds.—The aquohydroxobis(ethylenediamine)cobalt(III) compounds were prepared in preference to the diaquo compounds used by Bjerrum and Rasmussen, which are difficult to prepare and purify because of their great solubility. The aquohydroxo ions are converted to the diaquo ions on dissolution in acidic media.

trans-[Co(en)$_2$(H$_2$O)(OH)](ClO$_4$)$_2$.—*trans*-Aquohydroxobis(ethylenediamine)cobalt(III) perchlorate was prepared as described previously.[6] *Anal.* Calcd for [Co(en)$_2$(H$_2$O)(OH)](ClO$_4$)$_2$: Co, 14.3. Found: Co, 13.9.

cis- and *trans*-[Co(en)$_2$(H$_2$O)(OH)]Br$_2$.—The *cis* salt was prepared by the method of Werner[8] and recrystallized from 2 *M* hydrobromic acid. When the pH was raised to 4–5 by addition of potassium hydroxide pellets, some *trans* salt precipitated and was filtered off. The pH of the filtrate was then immediately raised to 7–8, causing precipitation of the *cis* salt. *Anal.* Calcd for *trans*-[Co(en)$_2$(H$_2$O)(OH)]Br$_2$: Br, 42.7; Co, 15.8; N, 15.0. Found: Br, 43.1; Co, 15.5; N, 14.7. Calcd for *cis*-[Co(en)$_2$(H$_2$O)(OH)]Br$_2$·H$_2$O: Br, 40.8; Co, 15.0. Found: Br, 41.0; Co, 14.7.

Spectrophotometric Solutions.—The nitrate and perchlorate solutions were both prepared by dissolving weighed amounts of the *cis*- and *trans*-aquohydroxobis(ethylenediamine)cobalt(III) bromides in enough 0.2 *M* nitric or perchloric acid to make the

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final diluted solutions 0.08 *F* in acid. Equivalent amounts of silver nitrate or perchlorate were added and the mixtures were allowed to digest for 1 hr or more. The precipitates were filtered off and washed and the filtrate and washings were treated with sodium nitrate or perchlorate, diluted to volume, and allowed to equilibrate in the dark for 1 week at 23 ± 1°.

Potentiometric Solutions.—A 4.9567-g sample (0.01200 mol) of *trans*-[Co(en)$_2$(H$_2$O)(OH)](ClO$_4$)$_2$ was dissolved in 0.01350 mol of 0.3 *M* perchloric acid and divided into two 250-ml volumetric flasks. One sample was made 1.00 *F* in sodium nitrate; the other, 1.00 *F* in sodium perchlorate before being placed in the dark to equilibrate for 1 week at 23 ± 1°.

Pmr Solutions.—Solutions were made approximately 1 *M* in the *cis* or *trans* cobalt salt by dissolving the solid perchlorate in 2 *M* perchloric or 3 *M* nitric acid and allowed to equilibrate in the dark at 23° for 1 week.

Equipment.—Spectrophotometric measurements of the 0.0100 *M* solutions were made on a Beckman DB spectrophotometer; those of the 0.00700 *M* solutions, on a Beckman DU spectrophotometer. The 100% transmittance standard in each case was a solution containing the same concentration of acid and salt (sodium nitrate or perchlorate) as the sample. Measurements were made at 492 mμ at room temperature (23 ± 1°).

Potentiometric measurements were made on a Beckman Research pH meter, Model 1019, standardized at pH 4.01 and 6.86. For use in the perchlorate solutions, the potassium chloride in the calomel electrode was replaced with saturated sodium chloride solution.[9] The 50-ml aliquots of each cobalt solution were treated according to the procedure described by Bjerrum and Rasmussen.[1]

Pmr measurements were made on a Varian A-60 spectrometer at the University of Nebraska in accordance with procedures already described.[6]

Results and Discussion

The potentiometric measurements were treated by appropriate modifications of the equations of Bjerrum and Rasmussen and are presented in Table I, using the notation of these authors. Within the limits of the method, the finding of 1 mol % *trans* ion in nitrate medium agrees with the 2 mol % reported by Bjerrum and Rasmussen. The principal uncertainties in the determination of the ratio in either ionic medium do not apply to the difference between the two ratios since the aliquots for both determinations came from the same solid cobalt salt and were subject to identical errors in acid concentration, etc. Thus, the amount of *trans* ion in the perchlorate medium is probably between 2 and 4 mol % and almost certainly 2 mol % more than in the nitrate medium.

Spectrophotometric results are presented in Table II. To permit ready comparison, samples 1–8 were made up to the same concentration of cobalt salt (0.0100 *M*) as that used by Bjerrum and Rasmussen, while samples 9–16 were made more dilute to minimize error in the absorbance measurements.

The absorbances of the solutions prepared from the *trans* salt are, in general, slightly higher than those from the *cis* salt, reflecting a difference in purity of the two salts. However, samples 4 and 8 both yield a molar absorptivity of 80.4, compared with 81.0 reported by Bjerrum and Rasmussen for a solution of the same approximate composition.

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TABLE I

TREATMENT OF 50.00-ml SAMPLES OF 0.02400 *M* DIAQUOBIS(ETHYLENEDIAMINE)COBALT(III) ION IN 1 *M* NITRATE AND PERCHLORATE MEDIA WITH NaOH AND THE CALCULATION OF THE *cis*:*trans* RATIO

pH	Amt of NaOH,[a] g	Vol, ml	c_{Co}, *M*	Log $(1 - \bar{v})$[b]	Log $(1 + \Delta)$[c]	pK_{a_1} (gr)	% *trans* ion
			Sodium Nitrate				
5.942	4.915	54.90	0.02186	−0.014	0.009	5.937	0.8
5.918	4.854	54.83	0.02189	−0.001	0.008	5.925	0.9
5.931	4.867	54.85	0.02188	−0.004	0.009	5.936	0.8
			Sodium Perchlorate				
5.742	4.830	54.81	0.02189	+0.005	0.006	5.753	2.6
5.747	4.881	54.86	0.02187	−0.007	0.006	5.746	2.7
5.732	4.877	54.86	0.02187	−0.006	0.005	5.731	2.9

[a] c_{NaOH} = 0.1546 equiv/1000 g of solution; ρ = 1.004 g/ml at 23°. [b] $\bar{v}$ = {[(equiv of NaOH − 0.00300)/vol] + [H$^+$]}/c_{Co}. [c] $\Delta = (2 - \bar{v})K_{a_2}(\mathrm{gr})/(1 - \bar{v})[\mathrm{H}^+]$.

TABLE II

ABSORPTIVITIES OF EQUILIBRIUM SOLUTIONS OF DIAQUOBIS(ETHYLENEDIAMINE)COBALT(III) ION IN NITRATE AND PERCHLORATE MEDIA AT 492 mμ AND 23°

No.	Sample	Acid (0.08 *F*)	Salt (1.0 *F*)	Absorbance	Absorptivity
1	0.0100 *M cis*	HClO$_4$	None	0.772	77.2
2	0.0100 *M cis*	HClO$_4$	NaClO$_4$	0.770	77.0
3	0.0100 *M cis*	HNO$_3$	None	0.775	77.5
4	0.0100 *M cis*	HNO$_3$	NaNO$_3$	0.804	80.4
5	0.0100 *M trans*	HClO$_4$	None	0.775	77.5
6	0.0100 *M trans*	HClO$_4$	NaClO$_4$	0.775	77.5
7	0.0100 *M trans*	HNO$_3$	None	0.780	78.0
8	0.0100 *M trans*	HNO$_3$	NaNO$_3$	0.804	80.4
9	0.00700 *M cis*	HClO$_4$	None	0.532	76.0
10	0.00700 *M cis*	HClO$_4$	NaClO$_4$	0.538	76.9
11	0.00700 *M cis*	HNO$_3$	None	0.542	77.4
12	0.00700 *M cis*	HNO$_3$	NaNO$_3$	0.553	79.0
13	0.00700 *M trans*	HClO$_4$	None	0.539	77.0
14	0.00700 *M trans*	HClO$_4$	NaClO$_4$	0.541	77.3
15	0.00700 *M trans*	HNO$_3$	None	0.547	78.1
16	0.00700 *M trans*	HNO$_3$	NaNO$_3$	0.562	80.3

Comparisons of samples 1 and 2, 5 and 6, 9 and 10, and 13 and 14 indicate that the presence of sodium perchlorate in the solutions causes no change in absorbance of the cobalt ion at 492 mμ. Comparison of these samples with the others shows unequivocally that the absorbance is increased by the presence of nitrate ion. The question arises as to whether this increased absorbance is due to a greater amount of *cis* ion or possibly to spectral changes accompanying coordination of the nitrate ion. Complete visible spectra of the various solutions offer no evidence of such coordination, although this does not preclude the possibility.

If one assumes that the differences in absorptivity indicate varying amounts of *cis* ion as suggested by the potentiometric measurements, then it is still difficult to obtain an accurate estimate of the absolute amount of *trans* ion, which is small in all of the solutions. However, the differences in absorptivity between the 1.00 *M* perchlorate solutions and the 1.00 *M* nitrate solutions are consistently present and outside the range of experimental error. These differences permit calculation of the change in the amount of *trans* ion

caused by the nitrate ion, using molar absorptivities of 80.9 and 19.2 reported by Bjerrum and Rasmussen for the pure *cis* and *trans* isomers. Comparison of samples 2 and 4 yields $(80.4 - 77.0)100/(80.9 - 19.2)$ or 5.5 mol % more *trans* ion in the nitrate solution than in the perchlorate. The other three pairs of samples—6 and 8, 10 and 12, and 14 and 16—yield, respectively, 4.7, 3.4, and 4.9 more mol %.

Integration of the methylene proton peak areas in the pmr spectra[6] of the equilibrium mixtures indicated 4 ± 2 mol % *trans* ion in 2 *M* perchloric acid. In 3 *M* nitric acid, the *trans* ion could not be detected. Both *cis* and *trans* salts gave the same equilibrium results.

Nitric acid causes a significant rearrangement of the amino proton peaks from their positions in perchloric acid solution; the peak representing the amino groups *trans* to each other divides with half of it moving downfield 0.6 ppm while the entire peak representing the amino groups *trans* to aquo groups moves downfield 0.3 ppm. Sulfuric and hydrobromic acids produce similar changes of less magnitude, the positions varying with acid concentration as reported by Fung.[10]

The deshielding of amino proton peaks in such complex ions by anions has been recently interpreted by Millen and Watts[11] to indicate ion association, possibly through proton bridges which lock the amino protons into axial and equatorial positions. The perchlorate ion reportedly does not engage in hydrogen bonding[12] and consequently only one peak, however broad, is evident for the amino protons *trans* to each other in perchlorate solution.

Acknowledgment.—This research was supported by a grant through the Mankato State College Faculty Research Council.

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On the Complex Formation of Chlorine Pentafluoride with Lewis Acids and Bases

BY KARL O. CHRISTE AND DONALD PILIPOVICH

Chlorine mono-, tri-, and pentafluorides are known to exist. Of these the first two compounds show amphoteric character and form ionic complexes with strong Lewis acids and bases. Thus, ClF forms with strong Lewis acids the FCl_2^+ cation[1] and with strong

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Lewis bases the ClF_2^- anion.[2–4] Similarly, the ClF_2^+ cation[5–12] and ClF_4^- anion[13–18] have been prepared from ClF_3. In spite of the fact that the existence of ClF_5 was published[19] 5 years ago, no data have been published on its complex formation with Lewis acids and bases. In this paper we wish to report on the preparation and some properties of adducts derived from ClF_5.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a well-seasoned 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 4251F4Y). Chlorine pentafluoride (prepared in this laboratory[20]) was purified by fractional condensation and stored in a stainless steel cylinder over dry CsF. Prior to use, the ClF_5 was purified once more by fractional condensation. Nitrosyl fluoride was prepared from NO and F_2 at $-196°$ and purified by fractional condensation. Arsenic pentafluoride (from Ozark-Mahoning Co.) and BF_3 (from The Matheson Co., Inc.) were purified by several low-temperature vacuum distillations. Antimony pentafluoride (from Ozark-Mahoning Co.) was purified by vacuum distillation at ambient temperature. Hydrogen fluoride (from The Matheson Co., Inc.) was purified by removing all volatiles at $-196°$, exposing the residue at ambient temperature for 12 hr to a fluorine pressure of 2 atm followed by removal of all volatiles at $-196°$ *in vacuo*. Cesium fluoride (from K & K Laboratories) was dried by fusion in a platinum crucible. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra. Because of their hygroscopic nature, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

Preparation of $ClF_5 \cdot AsF_5$.—In a typical experiment, ClF_5 (51.65 mmol) and AsF_5 (43.27 mmol) were combined at $-196°$ in a U trap. The mixture was allowed to warm up slowly until melting and reaction occurred. When the pressure inside the trap reached 760 mm, the mixture was cooled again to $-196°$. This procedure was repeated several times until the reaction was complete. Unreacted ClF_5 (8.61 mmol) was recovered by distillation at $-78°$. Therefore, AsF_5 (43.27 mmol) had reacted with ClF_5 (43.04 mmol) in a mole ratio of 1:0.995, producing the complex $ClF_5 \cdot AsF_5$.

Preparation of $ClF_5 \cdot SbF_5$.—Antimony pentafluoride (104

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