ture interval is 7.5 kcal./mole. Use of values for w_0 in conjunction with the calculated values for K_D with the assumption that the total concentration of dinitrogen pentoxide, *i.e.*, molecular plus ionized, is equal to the concentration of water as evaluated by w_0 shows that the present rate data can be accounted for in terms of a first order decomposition of dinitrogen pentoxide if 3.2% of the dinitrogen pentoxide from the self-dissociation of the acid is in the molecular form at 65° and if 5.4% is in the molecular form at 70°.

In regard to the question of identifying molecular dinitrogen pentoxide in liquid nitric acid, Raman spectra[11] at $-15°$ gave no clear cut indication of lines for this species, although lines for nitronium ion and nitrate ion were evident. In order to see whether this Raman result is compatible with interpretation of the present kinetic data, a calculation was made for the equilibrium constant, K_i, for the ionization of dinitrogen pentoxide into nitronium and nitrate ions according to equations 4 and 5. Calculation of K_i was made assuming again that the total concentration of dinitrogen pentoxide was equal to w_0 as obtained from the kinetic studies. The concentration of the molecular species was obtained from the values of w_0 and K_D, the self-dissociation constant for nitric acid, as listed above. It was calculated in this fashion that at 65° K_i = 5.61 molal and at 70° K_i = 2.54 molal. The ΔE from these values for K_i is -36.6 kcal./mole. From these values K_i was calculated at $-15°$ and it was found that, although molecular dinitrogen pentoxide may exist in liquid nitric acid at elevated temperatures, at $-15°$ it should be essentially completely ionized. The result of this calculation, then, is compatible with the experimental result that the molecular species was not identified in Raman spectra for nitric acid solution at $-15°$. The calculations also suggest, however, that Raman spectra should be obtained at higher temperatures in order to identify the molecular species. Such work should be attempted in order to test experimentally the estimates of the molecular species calculated from the present kinetic study.

Acknowledgments.—It is a pleasure to acknowledge the assistance given this study by several members of the laboratory. D. Moore designed the thermistor bridge circuit for the constant temperature bath and Helen R. Young and A. V. Jensen carried out the mass spectrometric analysis of the decomposition gases. Mrs. Ethel Kaufman assisted with some of the kinetic runs.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions of Complex Ions. VIII. Hydrolysis of *cis*- and *trans*-Chlorohydroxo-bis-(ethylenediamine)-cobalt(III) Complexes[1,2]

BY RALPH G. PEARSON, ROBERT E. MEEKER AND FRED BASOLO

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The rates of reaction of *cis*- and *trans*-chlorohydroxo-bis-(ethylenediamine)-cobalt(III) complexes with water are reported. They are considerably faster than those of the corresponding dichloro complexes. A discussion is given of the products of reaction of one mole of hydroxide ion with one mole of *cis*- or *trans*-$[\mathrm{Coen_2Cl_2}]^+$.

An examination of the literature showed that there was no report of a direct measurement of the rate of aquation of a chlorohydroxo complex ion of cobalt(III). These compounds are, in fact, unknown in the solid form and can only be prepared in solution where they have a limited life-time. It is necessary therefore to study their reaction *in situ* directly after formation.

We have made several chlorohydroxo complexes in solution by adding a limited amount of alkali to an aqueous solution of the corresponding chloroaquo or dichloro complex. The rate of aquation of the remaining chloro group was then determined immediately by potentiometric titration. The *cis*-isomer of chloroaquobis-(ethylenediamine)-cobalt(III) is known but it has not been possible to isolate the *trans*-form.[3] It is assumed that a proton transfer on adding one equivalent of alkali leaves the configuration unchanged and thus readily furnishes the *cis*-chlorohydroxo in solution

$$cis\text{-}\mathrm{Coen_2ClH_2O^{+2}} + \mathrm{OH^-} \longrightarrow cis\text{-}\mathrm{Coen_2ClOH^+} + \mathrm{H_2O} \quad (1)$$

To prepare and study the *trans*-chlorohydroxo complex it is necessary to start with a dichloro complex.

When one equivalent of hydroxide ion is added to a solution of a dichloro complex a very complicated system results. Initially hydroxide ion is consumed according to equation 2 to form the chlorohydroxo complex. Both the *cis*- and *trans*-chlorohydroxo complexes may be formed.

$$[\mathrm{Coen_2Cl_2}]^+ + \mathrm{OH^-} \xrightarrow{k_1} [\mathrm{Coen_2ClOH}]^+ + \mathrm{Cl^-} \quad (2)$$

These products then compete with the dichloro complex for the remaining hydroxide ion, forming the *cis*- and *trans*-dihydroxo complexes, as illustrated in equation 3. Reaction (3) is nearly as rapid as reaction (2), as shown by a comparison of rate constants k_1 and k_2 in reference 1

$$[\mathrm{Coen_2ClOH}]^+ + \mathrm{OH^-} \xrightarrow{k_2} [\mathrm{Coen_2(OH)_2}]^+ + \mathrm{Cl^-} \quad (3)$$

so that an appreciable concentration of the dihydroxo complex is formed.

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[1] For previous papers in this series see R. G. Pearson, R. E. Meeker and F. Basolo, THIS JOURNAL, **78**, 709 (1956).

[2] This investigation supported by the U. S. Atomic Energy Commission under Contract AT(11-1)89, Proj. No. 2.

[3] A. Werner, *Lieb. Ann.*, **386**, 17 (1912).

Thus, when all the hydroxide ion has been consumed, there still remains an amount of unreacted dichloro complex equivalent to the amount of dihydroxo complex formed. The consumption of hydroxide ion is normally complete within a fraction of a second. After the hydroxide ion has been consumed there still remain three reactive species which aquate with half-times ranging from several seconds to several minutes. These reactive species are the *cis*- and *trans*-chlorohydroxo complexes and the unreacted dichloro complex. The aquation of this dichloro complex creates still another, but much less reactive species, the chloroaquo complex.

Despite the complexity of the system, it is possible to unravel it and extract the rates of aquation of the several species involved. The procedure used is described below.

Experimental and Results

Solutions 2×10^{-3} *M* in dichloro complex and in hydroxide ion were thermostated at 25°. Aliquots of the reaction mixture were withdrawn at suitable intervals and analyzed for ionic chloride by a potentiometric technique to be described elsewhere.[4]

A first-order plot of the data was initially curved, but eventually became linear. This linear region is attributed to the aquation of the dichloro complex after the more rapid aquations of the chlorohydroxo complexes were complete. Since this dichloro complex eventually liberates two equivalents of chloride ion, a small correction was applied to the experimental V_∞ to obtain the value appropriate to the liberation of the first chloro group only. This correction was first estimated and then refined from the composition data mentioned below.

The contributions from this slow component were subtracted by the method of Brown and Fletcher[5] to obtain a linear plot for the component of intermediate rate, which is designated as one of the isomeric chlorohydroxo complexes. Figure 1 shows these plots for the system derived from *cis*-$[\mathrm{Coen_2Cl_2}]^+$.

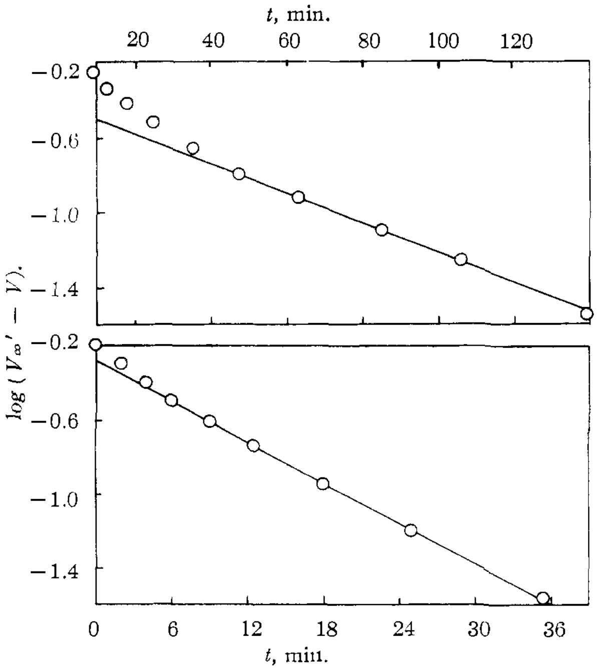

Fig. 1.—Plots of kinetic data observed after reaction of one equivalent of NaOH with 0.002 *M* *cis*-$\mathrm{Co(en)_2Cl_2^+}$ at 25°. Lower curve derived from upper curve by correcting V_∞ for amount of dichloro complex.

The second plot is still curved for the first three or four minutes. It is believed to be the aquation of the other isomeric chlorohydroxo complex which is responsible for this initial curvature. An attempt was made to estimate the rate constant for this rapid component by subtracting the contributions from the intermediate component. Not enough titration data could be obtained during the first few minutes of reaction for any reliable determination, but the order of magnitude of the rate constant could be estimated from the data. An attempt was also made to study the rate of the rapid reaction by the flow method described in an earlier paper.[1] However, the reaction was too slow for this method and again only the order of magnitude could be found.

Table I summarizes the rate constants obtained by these methods. The aquation rates were obtained from the slopes of linear plots such as those shown in Fig. 1.

Table I

Aquation Rates Observed after Reaction of One Equivalent of Hydroxide Ion with Dichloro Complexes at 25°

Initial complex[b]	k (sec.$^{-1}$) Dichloro	k (sec.$^{-1}$) slow-ClOH	k (sec.$^{-1}$) fast-ClOH
cis-$[\mathrm{Coen_2Cl_2}]^+$	3.1×10^{-4}	1.43×10^{-3}	8×10^{-3}
trans-$[\mathrm{Coen_2Cl_2}]^+$	1.1×10^{-4}	1.45×10^{-3}	8×10^{-3}[a]
trans-$[\mathrm{Copn_2Cl_2}]^+$	2.2×10^{-4}	1.3×10^{-3}	....

[a] Flow method gives $k = 3.6 \times 10^{-2}$ sec.$^{-1}$, but experimental difficulties make this value unreliable. [b] en = ethylenediamine; pn = propylenediamine.

The aquation rates for the dichloro complexes are in agreement with those calculated from previous data[1] since the *p*H of the system levels out between 6 and 7. Table II illustrates the way in which the *p*H changes with time after one equivalent of NaOH is added to an aqueous solution of *trans*-$[\mathrm{Coen_2Cl_2}]^+$ at 25°. Similar *p*H changes are observed using the other dichloro complexes. At a *p*H of 7 more than half of the hydrolysis of the dichloride proceeds through reaction with hydroxide ion. However, the value of k_2 in equation 3 is small enough, and the rate of direct reaction of the chlorohydroxo complexes with water is large enough so that no correction for hydroxide ion reaction needs to be made at *p*H 7 for the chlorohydroxo complexes.

Table II

*p*H	*t* (min.)	*p*H	*t* (min.)
8.73	0.75	7.27	10.0
8.33	1.25	7.08	18.0
8.00	2.0	6.98	25.0
7.52	5.0		

The percentages of the various components in the system can be calculated from the intercepts of linear plots such as those shown in Fig. 1. The percentage of dichloro complex (and, consequently, of dihydroxo complex) can also be predicted independently from a knowledge of the ratio, $K = k_2/k_1$, of the rate constants for reactions (3) and (2) by applying successive approximations to solve equation 4, where

$$F = (1 - K - F^K)/(1 - 2K) \qquad (4)$$

F is the fraction of dichloro complex left after the consumption of one equivalent of hydroxide ion.[6] The rate constants k_1 and k_2 were both determined by the flow technique, and are reported for several complexes in reference 1.

Table III lists the percentages calculated from (4) for the dichloro component and the percentages found for all components from the experimental data.

The preparation of *cis*-$[\mathrm{Coen_2ClOH}]^+$ was carried out in two ways. In the first of these, one equivalent of NaOH was added to an aqueous solution 0.002 *M* in *cis*-$[\mathrm{Coen_2ClH_2O}]^{+2}$.[3] The product immediately formed is assumed to be *cis*-$[\mathrm{Coen_2ClOH}]^+$, since a proton transfer would not be expected to involve any change in configuration. The

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(4) P. M. Henry, Thesis, Northwestern University, 1956.

(5) H. C. Brown and R. S. Fletcher, This Journal, **71**, 1845 (1949).

(6) F. H. Westheimer, W. A. Jones and R. A. Lad, *J. Chem. Phys.*, **10**, 478 (1942).

TABLE III

PERCENTAGES OF THE VARIOUS COMPONENTS FOUND AFTER REACTION OF ONE EQUIVALENT OF HYDROXIDE ION WITH SOME DICHLORO COMPLEXES AT 25°

Initial complex	Calcd. $[\mathrm{Coen_2Cl_2}]^+$	Found $[\mathrm{Coen_2Cl_2}]^+$	Found $[\mathrm{Coen_2(OH)^{-2}}]^+$	Found $[\mathrm{Coen_2ClOH}]^+$ *trans*-	Found $[\mathrm{Coen_2ClOH}]^+$ *cis*-
cis-$[\mathrm{Coen_2Cl_2}]^+$	..	20.6	20.6	50.2	8.5
trans-$[\mathrm{Coen_2Cl_2}]^+$	9[a]	13.8	13.8	54.7	17.7
trans-$[\mathrm{Copn_2Cl_2}]^+$	11[b]	11.3	11.3	41.6	35.9

[a] $k_1 = 3.0 \times 10^3$ mole^{-1} sec.$^{-1}$ and $k_2 = 2.0 \times 10^2$ mole^{-1} sec.$^{-1}$. [b] $k_1 = 2.3 \times 10^3$ mole^{-1} sec.$^{-1}$ and $k_2 = 2.1 \times 10^2$ mole^{-1} sec.$^{-1}$. Data taken from reference 1.

subsequent aquation of this product was followed by potentiometric titration of chloride ion. More than 75% of the total chloride was liberated within three minutes after the addition of the base, and essentially all of the chloride was liberated within about 20 minutes.

A first-order plot of the titration data was not linear, indicating that a mixture of isomers was present. The initial slope corresponded to a rate of 1.0×10^{-2} sec.$^{-1}$. No limiting straight line portion was obtained because the slower component was present in small amounts only (estimated to be about 8%).

In the second experiment a sample of *cis*-$[\mathrm{Coen_2Cl_2}]^+$ was allowed to react at *p*H 3 and 25° for 170 minutes, thus giving a solution of the chloroaquo complexes. Then one equivalent of hydroxide ion was added to convert the aquo complexes to hydroxo complexes, and the subsequent reactions were followed by potentiometric titration of chloride ion.

Mathieu[7] has shown that the optically active *cis*-dichloro complex aquates in acidic solution with retention of configuration. He reports that the rate of loss of optical activity is one-tenth as fast as the rate of aquation. This loss in activity may result either from the formation of a *trans*-chloroaquo product or from the formation of a racemic mixture of *cis*-chloroaquo products. Thus, the rate of formation of *trans*-chloroaquo complex is at most one tenth the rate of aquation.

Letting the reaction sequence be represented schematically by

$$\mathrm{A} \xrightarrow{k} \mathrm{B} \xrightarrow{k'} \mathrm{C} \qquad (5)$$

where A = *cis*-dichloro, B = *cis*-chloroaquo and C = *trans*-chloroaquo, and letting $K = k'/k = 0.1$, then we may write[8]

$$B_{\max} = A_0 K^{K/(1-K)} \text{ and } t_{\max} = \frac{1}{k(K-1)} \ln K \qquad (7)$$

where $t_{\max}$ is the time at which the concentration of component B is a maximum, and where $B_{\max}$ is the maximum concentration of component B. For A = *cis*-$[\mathrm{Coen_2Cl_2}]^+$ $t_{\max}$ is 170 minutes (about four half-lives for the aquation of A), and $B_{\max}$ is $0.77\,A_0$ at 25°.

Thus, in the second experiment described above the products obtained after 170 minutes of reaction should include at least 77% of the *cis*-isomer and at most 23% of the *trans*-isomer. The addition of one equivalent of NaOH would be expected to yield the same percentages of the corresponding chlorohydroxo complexes, because no change in configuration is expected for a proton transfer. The first-order plot of the data for the aquation of these chlorohydroxo complexes indeed indicated a mixture of two components, the rapid component comprising 79% of the mixture and the slow component comprising 21% of the mixture. The rate constant obtained for the slow component was 1.4×10^{-3} sec.$^{-1}$, in agreement with the value reported in Table I. The contributions from this slow component were subtracted by the method of Brown and Fletcher[5] to obtain a linear plot for the fast component. The rate constant obtained in this way was 1.3×10^{-2} sec.$^{-1}$. This value is considered to be much more reliable than that obtained by the other methods mentioned earlier.

Discussion

The experiments on the rates of hydrolysis and amounts of the products formed by adding one equivalent of alkali to the two preparations of *cis*-chloroaquo complex permit a clear assignment of rates to the two isomeric chlorohydroxo complexes. The more rapidly reacting isomer in Table I is the *cis*- and the more slowly reacting isomer is the *trans*-. The *cis*-chloroaquo complex prepared by the method of Werner is apparently about 92% *cis* and 8% *trans*.

The good agreement between the calculated (77%) and found (79%) amount of *cis*-isomer in the second method of preparation (aquation of *cis*-dichloro followed by alkali) confirms the assignment. It also proves that the mechanism of loss of optical activity from the *cis*-chloroaquo complex involves isomerization to the *trans*-isomer and not racemization.

The literature contains some other information on rates of reaction of chlorohydroxo complexes of cobalt(III). Brönsted[9] reports that the aquation rate constant for *cis*-$\mathrm{Co(NH_3)_4H_2OCl^{+2}}$ at 20° is given by

$$k = 2.17 \times 10^{-6} + 2.67 \times 10^{-8}/[\mathrm{H^+}] \qquad (8)$$

and that the aquation rate constant for *cis*-$\mathrm{Co(NH_3)_4NO_3H_2O^+}$ at 20° is given by

$$k = 2.5 \times 10^{-5} + 5.33 \times 10^{-7}/[\mathrm{H^+}] \qquad (9)$$

in units of sec.$^{-1}$. Brönsted interprets the first term in each case as the contribution of the aquo complex and the second term as the contribution of the hydroxo complex. Thus, an analytical expression for the rate constant might be

$$k = k_{\mathrm{H_2O}} + k_3K_a/[\mathrm{H^+}] \qquad (10)$$

where k_3 is the rate constant for aquation of the chlorohydroxo complex, and K_a is the acid dissociation constant for the parent aquo complex.[10]

The K_a value for the chloroaquo complex is unknown, but it can be estimated to be of the order of 10^{-8}. For example, the K_a value reported in reference 1 for $[\mathrm{Coen_2OHH_2O}]^{+2}$ is 1.4×10^{-8}. This estimate for K_a would give a value of k_3 of about 2.7 sec.$^{-1}$ for (8).

A similar analysis of the data of Mathieu[11] for

TABLE IV

COMPARISON OF THE AQUATION RATES OF SOME HYDROXO COMPLEXES WITH THE CORRESPONDING CHLORO COMPLEXES AT 25°

Complex	k (sec.$^{-1}$)	Ratio
trans-$[\mathrm{Coen_2ClOH}]^+$	1.4×10^{-3}	
trans-$[\mathrm{Coen_2Cl_2}]^+$	3.2×10^{-5}	44
cis-$[\mathrm{Coen_2ClOH}]^+$	1.3×10^{-2}	
cis-$[\mathrm{Coen_2Cl_2}]^+$	2.5×10^{-4}	52
cis-$[\mathrm{Co(NH_3)_4ClOH}]^+$	2.7[a]	
cis-$[\mathrm{Co(NH_3)_4Cl_2}]^+$	(2×10^{-2})[b]	130
trans-$\mathrm{Copn_2ClOH^+}$	1.3×10^{-3}	
trans-$\mathrm{Copn_2Cl_2^+}$	6.2×10^{-5}	21

[a] Estimated only, see text. [b] Estimated from rate of reaction of *trans*-$\mathrm{Co(NH_3)_4Cl_2^+}$ and ratio of rates of *cis*- and *trans*-$\mathrm{Coen_2Cl_2^+}$. The direct rate is too fast to measure.

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(7) J. P. Mathieu, *Bull. soc. chim.*, **4**, 683 (1937).

(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 155.

(9) J. N. Brönsted, *Z. physik. Chem.*, **122**, 383 (1926).

(10) Another possible interpretation of the second term of equation 8 is that it represents a reaction of the chloroaquo complex with hydroxide ion. The rate constant required for this to be true is far too large to be plausible.

(11) J. P. Mathieu, *Bull. soc. chim.*, [5] **3**, 2121 (1936).

the aquation of *cis*-$[\mathrm{Coen_2ClH_2O}]^{+2}$ at 30° in various buffers leads to

$$k = 3 \times 10^{-5} + 1 \times 10^{-9}/[\mathrm{H}^+]\ \mathrm{sec.}^{-1} \quad (11)$$

This result is in agreement with the value of k_3 (aquation of the *cis*-chlorohydroxo complex) found in this work provided that K_a is taken as about 4×10^{-8}, allowing a factor of two in rate constants for the five degree temperature difference.

Mathieu also reports an experiment similar to the one described in connection with Table I in which he adds one equivalent of NaOH to a solution of *cis*-$[\mathrm{Coen_2Cl_2}]^+$, and follows the subsequent kinetic processes. He reports $k = 7.7 \times 10^{-4}$ sec.$^{-1}$ at 30° for the aquation of the chlorohydroxo complex. This value is too low for he failed to account for the large amount of dichloro complex remaining in the reaction mixture and for the mixture of isomers.

Table IV shows the final assignment of rate constants for several chlorohydroxo complex ions. For comparison the rate constants for acid hydrolysis of the corresponding dichloro complexes are included. It is seen that, even though the electrical charges on the ions are the same, the chlorohydroxo complexes react 20–100 times faster than the dichloro complexes in spite of the statistical factor of two favoring the latter. It is also noteworthy that like the dichloro complexes of bis-(ethylenediamine)–cobalt(III) ion, the *cis*-chlorohydroxo ion reacts faster than the *trans*-isomer.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions of Complex Ions. IX. Contribution of Inductive Effects to the Rates of Acid and Base Hydrolysis of Cobalt(III) Complexes[1,2]

BY FRED BASOLO, JOHN G. BERGMANN, ROBERT E. MEEKER AND RALPH G. PEARSON

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Rates of acid and base hydrolysis have been measured for a series of $[\mathrm{Coen_2X\text{-}pyCl}]^{+2}$ complexes. The rates of acid hydrolysis increase with increasing base strength of X-py whereas that of base hydrolysis decreases. Inductive factors contribute less than do steric factors to the rates of reaction of cobalt(III) complexes. These results are discussed in terms of the mechanisms for acid and base hydrolysis reactions.

The rate of acid hydrolysis (aquation) of cobalt(III) complexes was shown to increase with increasing size of the "inert" ligands. The greater rate of reaction of the more sterically hindered complexes is cited in support of a dissociation mechanism (S_N1).[3] Thus, in a series of complex ions containing substituted ethylenediamine such as *trans*-$[\mathrm{Co(AA)_2Cl_2}]^+$, an alkyl substituent increases the rate of aquation. Although the accelerated rate has been attributed to steric factors, it is also possible that this may result from the inductive effect of the alkyl group, piling up negative charge on the cobalt atom and hence repelling the chloride ion.[4] It is therefore necessary to have some estimate of the contribution of both steric and inductive effects to the speed of these reactions. The object of this investigation is to determine the rates of acid and base hydrolysis for some cobalt(III) complexes with ligands of different base strengths but of approximately the same steric requirements.

Experimental

Preparation of Compounds.—The method described by Bailar and Clapp[5] was used to prepare the substituted pyridine complexes $[\mathrm{Coen_2X\text{-}pyCl}]\mathrm{Cl_2}$. These salts were dried in a desiccator over potassium hydroxide and analyzed for nitrogen and ionic chloride.

Compound[a]	Ionic chlorine, % Calcd.	Ionic chlorine, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
$[\mathrm{Coen_2pyCl}]\mathrm{Cl\cdot H_2O}$	18.5	18.3	18.5	18.3
$[\mathrm{Coen_2}\beta\text{-}\mathrm{CH_3\text{-}pyCl}]\mathrm{Cl_2}$	18.7	18.6	18.5	17.9
$[\mathrm{Coen_2}\gamma\text{-}\mathrm{CH_3\text{-}pyCl}]\mathrm{Cl_2}$	18.7	18.3	18.5	18.2
$[\mathrm{Coen_2}\gamma\text{-}\mathrm{OCH_3\text{-}pyCl}]\mathrm{Cl_2}$	17.9	17.9	17.7	18.3

[a] en = ethylenediamine, py = pyridine, β-$\mathrm{CH_3}$-py = β-picoline, γ-$\mathrm{CH_3}$-py = γ-picoline, γ-$\mathrm{OCH_3}$-py γ-methoxypyridine. The geometric configuration of these complexes is not known. However as they were all prepared by the same method and they all have their similar absorption spectra, it is believed that they all have the same structure.

Attempts to prepare compounds containing pyridine substituted with electron attracting groups were not successful. The pyridine derivatives used were 3- and 4-cyanopyridine, nicotinic acid and nicotinamide. In no case did the pyridine appear to coördinate and the only product isolated from these reaction mixtures was *cis*-$[\mathrm{Coen_2Cl_2}]\mathrm{Cl}$. Bailar and Clapp[5] report similar observations for reactions of several other weak bases.

trans-Dichloro-tetrakis-(pyridine)-cobalt(III) nitrate was prepared by the method of Werner and Feenstra.[6] Analogous compounds containing β- and γ-picoline were prepared by this same method. These nitrate salts were recrystallized from water, washed with ether, dried overnight in a desiccator over drierite, and analyzed for chlorine and nitrogen.

Compound	Chlorine, % Calcd.	Chlorine, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
$[\mathrm{Copy_4Cl_2}]\mathrm{NO_3}$	14.0	13.8	13.8	14.1
$[\mathrm{Co(}\beta\text{-}\mathrm{CH_3\text{-}py)_4Cl_2}]\mathrm{NO_3\cdot 3H_2O}$	11.5	11.3	..	..
$[\mathrm{Co(}\gamma\text{-}\mathrm{CH_3\text{-}py)_4Cl_2}]\mathrm{NO_3\cdot H_2O}$	12.2	12.0	11.9	12.2

The procedure described by Jaeger and Van Dyk[7] was employed to obtain *trans*-dichloro-bis-(2,2′-dipyridyl)-cobalt(III) chloride. The compound was dried overnight in a desiccator.

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[1] (1) For previous paper in this series see R. G. Pearson, R. E. Meeker and F. Basolo, THIS JOURNAL, **78**, 2673 (1956).

[2] (2) This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(11-1)-89-Project No. 2.

[3] (3) R. G. Pearson, C. R. Boston and F. Basolo, THIS JOURNAL, **75**, 3089 (1953).

[4] (4) D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2674 (1953).

[5] (5) J. C. Bailar, Jr., and L. B. Clapp, THIS JOURNAL, **67**, 171 (1945).

[6] (6) A. Werner and R. Feenstra, *Ber.*, **39**, 1538 (1906).

[7] (7) F. M. Jaeger and J. A. Van Dyk, *Z. anorg. allgem. Chem.*, **227**, 317 (1936).