78. *Mechanism and Steric Course of Octahedral Aquation. Part VII.* Aquation and Base Hydrolysis of a Chlorocyanobis(ethylenediamine)-cobalt*(III) *Isomer.*

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The aquation and base hydrolysis of one of the isomers, probably *trans*, of the $[\mathrm{Co\ en_2\ CN\ Cl}]^+$ cation have been studied. The aquation is slower, and the base hydrolysis is somewhat faster, than that of the corresponding chloronitro-complex, but the steric courses cannot be determined with certainty. The products of aquation, mercuric ion-catalysed aquation, and base hydrolysis (after acidification), all have the same spectrum, which is identical with that of the only isolated isomer of the $[\mathrm{Co\ en_2\ CN\ H_2O}]^{2+}$ cation. It is believed that all three reactions proceed with complete retention of configuration.

The study of the role of the non-participating ligand, A, in the aquation and base hydrolysis of complexes of the type, $[\mathrm{Co\ en_2ACl}]^{n+}$, has led to certain conclusions concerning the mechanisms of these reactions.[1] In most cases, the ligands studied can displace electrons towards the metal and so promote a unimolecular reaction. Information concerning electron-withdrawing groups is limited almost entirely to the complexes where A = $\mathrm{NH_3}$[2] or $\mathrm{NO_2}$[1a] and it was desirable to obtain information about other such systems. The cyanide ligand appears to fit into this category since it has potentially available empty orbitals to receive a pair of electrons from the d_ϵ-orbitals of the metal, and so the preparation of the *cis*- and the *trans*-isomer of the $[\mathrm{Co\ en_2\ CN\ Cl}]^+$ cation was attempted. One such isomer has now been prepared and identified,[3] and the kinetics and steric course of its aquation and base hydrolysis are reported in this paper. Attempts to prepare the other isomer were unsuccessful.

Aquation.—

$$[\mathrm{Co\ en_2\ CN\ Cl}]^+ + \mathrm{H_2O} \overset{k_1}{\rightleftharpoons} [\mathrm{Co\ en_2\ CN\ H_2O}]^{2+} + \mathrm{Cl}^-$$

The kinetics of the reaction were followed by studying the increase of the free chloride-ion concentration in the solution titrimetrically. The anionic chloride was separated from the complex cations by means of a cation-exchange resin and was determined by Volhard's method. The rate constants for aquation were determined from the slope of the plot of $\log_{10}(V_\infty - V_t)$ against time, where V_t is the titre of silver nitrate consumed when the reaction is stopped at time t, and V_∞ is that calculated for the displacement of all the

Table 1.

First-order rate constants for the aquation of chlorocyanobis(ethylenediamine)-cobalt(III) nitrate in neutral aqueous solution.

Initial [Complex] (mmole/l.)	10^5k_1 (sec.$^{-1}$)	Initial [Complex] (mmole/l.)	10^5k_1 (sec.$^{-1}$)	Initial [Complex] (mmole/l.)	10^5k_1 (sec.$^{-1}$)
At 0·0°		At 10·1°		At 25·4°	
2·03	0·227	2·08	1·04	2·04	8·3
3·91	0·226	4·06	1·04	4·15	8·3
6·05	0·226	6·08	1·03	6·04	8·3
7·89	0·225	8·02	1·03	7·60	8·3
				4·09 *	8·3
				8·07 *	8·3

* Complex provided as chloride.

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* Part VI, preceding paper.

[1] (*a*) Ingold and Ašperger, *J.*, 1956, 2862; (*b*) Pearson and Basolo, *J. Amer. Chem. Soc.*, 1956, **78**, 4878; Ingold, Nyholm, and Tobe, *Nature*, (*c*) 1960, **187**, 477; (*d*) 1962, **194**, 344.

[2] (*a*) Nyholm and Tobe, *J.*, 1956, 1707; (*b*) Tobe, *J.*, 1959, 3776.

[3] Chan and Tobe, *J.*, 1963, in the press.

co-ordinated chlorine. Titration of the reaction mixture after ten half-lives indicated that, when the complex was supplied as the nitrate, equilibrium was reached with 95% aquation. The first-order rate constants are given in Table 1 and follow a temperature-dependence of the form:

$$k = 2{\cdot}5 \times 10^{12} \exp(-22{,}600/\boldsymbol{R}T) \text{ sec.}^{-1}$$

Base Hydrolysis.—

$$[\mathrm{Co\ en_2\ CN\ Cl}]^+ + \mathrm{OH}^- \xrightarrow{k_1} [\mathrm{Co\ en_2\ CN\ OH}]^+ + \mathrm{Cl}^-$$

The complex reacts with alkali quite rapidly, releasing chloride ions and changing in colour from yellow-orange to yellow. At no stage during or after the reaction could free cyanide ions be detected in solution. The reaction was followed by a sampling method, whereby aliquot portions of the reaction mixture were withdrawn and delivered into vessels containing an excess of cooled dilute nitric acid. The ionic chloride was determined as described in Section (1). The reaction followed a second-order rate law, and the rate constants were calculated by one of the following integrated expressions, depending upon circumstance:

(a) Under normal conditions, $k_2 = \dfrac{2{\cdot}303}{t(b-a)} \log_{10} \dfrac{a(b-x)}{b(a-x)}$

(b) When $b \gg a$, $k_2 = \dfrac{2{\cdot}303}{tb} \log_{10} \dfrac{a}{a-x}$

(c) When $b = a$, $k_2 = \dfrac{1}{t(a-x)} - \dfrac{1}{ta}$

The values of k_2 in Table 2 represent the average of individual constants determined at different stages of a particular run, a and b represent the concentrations of complex and hydroxide at time $t = 0$, and x represents the observed increase in the concentration of free chloride ions between times $t = 0$ and t. At hydroxide concentrations greater than 10^{-2}M, the rate constant appeared to decrease, but the addition of a neutral salt showed this to be a primary salt effect and not a specific property of the hydroxide ion. The rate constants have the following temperature dependence:

TABLE 2.

Second-order rate constants for the base hydrolysis of chlorocyanobis(ethylenediamine)cobalt(III) nitrate in aqueous solution.

Initial [Complex] (mmole/l.)	Initial [OH⁻] (mmole/l.)	k_2 (sec.$^{-1}$ mole^{-1})	Initial [Complex] (mmole/l.)	Initial [OH−] (mmole/l.)	k_2 (sec.$^{-1}$ mole^{-1})	Initial [Complex] (mmole/l.)	Initial [OH−] (mmole/l.)	k_2 (sec.$^{-1}$ mole^{-1})
	At 0·0°			At 10·1°			At 25·4°	
1·05	10·0	0·129	1·05	10·0	0·63	1·02	1·02	5·4
2·06	10·0	0·128	2·07	10·0	0·63	2·05	2·05	5·2
3·08	10·0	0·127	3·07	10·0	0·62	3·04	3·04	5·1
4·08	10·0	0·126	4·05	10·0	0·62	3·96	3·96	4·9
6·07	6·07	0·128	4·03	4·03	0·65			
8·04	8·04	0·124						
4·05	100	0·093						
4·06	10·0	0·092 *						

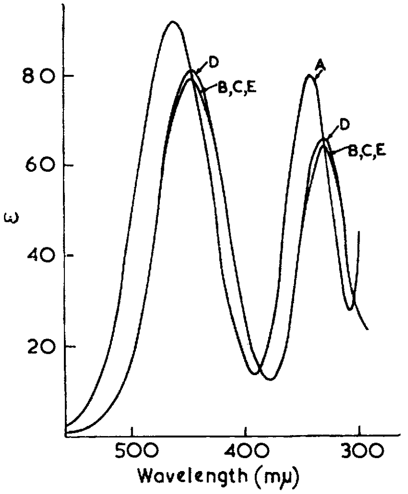
* Solution also $9{\cdot}0 \times 10^{-2}$M in $NaNO_3$.

$$k_2 = 5 \times 10^{17} \exp(-23{,}200/\boldsymbol{R}T) \text{ l.sec.}^{-1}\text{mole}^{-1}$$

(for an average ionic strength of 0·012M).

Steric Courses.—In spite of much effort it was possible to isolate only one isomeric form of the chlorocyano-complex and only one isomer of the aquocyano (or hydroxocyano)-complex. Assigning a configuration to a complex when only one isomeric form is available is always risky unless it happens to be the *cis*-isomer of an octahedral bischelated complex and can be resolved into optically active enantiomorphs. The configuration here assigned is based on the preparation of crystalline salts with resolving agents that cannot be separated by fractional crystallisation and on certain aspects of the infrared absorption spectra. This is discussed more fully elsewhere,[3] and it is concluded that a *trans*-configuration is indicated. Until both isomeric forms of the product have been characterised and the *cis*-isomer resolved, the steric courses of the aquation and the base hydrolysis cannot be ascertained with certainty, but, fortunately, circumstances have combined in these cases to allow some reasonable conclusions to be drawn. The following observations are of importance.

(*a*) The spectrum of an aqueous solution of the aquocyano-complex remains unchanged, apart from a small increase at 3000 Å, after 8 hours' heating at 80°, a time equal to 1000 half-lives for the aquation of the chloro-complex under comparable conditions. From this it can be assumed that either the rate of isomerisation is very slow or the solution at equilibrium contains very little of the other isomer. That the two isomers have identical spectra is very unlikely.



Spectra of the products of the solvolysis of *trans*-$[Co\ en_2\ CN\ Cl]^+$.

(A) *trans*-$[Co\ en_2\ CN\ Cl]NO_3$. (B) *trans*-$[Co\ en_2\ CN\ Cl]NO_3$ after ten half-lives of aquation. (C) *trans*-$[Co\ en_2\ CN\ Cl]NO_3$ + excess $Hg(ClO_4)_2$ after 15 minutes. (D) *trans*-$[Co\ en_2\ CN\ Cl]NO_3 + OH^-$; acidified after 10 minutes. (E) *trans*-$[Co\ en_2\ CN\ H_2O](ClO_4)_2$.

(*b*) The products of aquation, mercuric ion-catalysed aquation, and base hydrolysis were examined spectrophotometrically. Three solutions of the salt $[Co\ en_2\ CN\ Cl]NO_3$ were prepared, the first was set aside, the second was treated with 0·1M-mercuric perchlorate and 0·1M-perchloric acid, and the third was treated with an excess of sodium hydroxide solution and acidified when the reaction was complete. The spectra of these three solutions, together with the spectrum of a pure sample of $[Co\ en_2\ CN\ H_2O](ClO_4)_2$, are given in the Figure. All four spectra are very similar and it has been concluded that, unless the spectra of the two isomers of the product are virtually identical, all three reactions give only one isomer of the product. Within the limits of reliability of the assignment of configuration to the complexes used, aquation and mercuric ion-catalysed, and base hydrolysis of *trans*-$[Co\ en_2\ CN\ Cl]^+$ proceed with almost complete retention of configuration.

Discussion.—The rates, Arrhenius parameters, and steric courses of aquation and base hydrolysis of *trans*-$[Co\ en_2\ CN\ Cl]^+$ are collected in Table 3 where they are compared with the corresponding values for the ion *trans*-$[Co\ en_2\ NO_2\ Cl]^+$. Although base hydrolysis of the cyano-complex is somewhat faster than that of the nitro-complex, the rate of aquation is some 12 times slower. This lesser labilising power of the cyano- than of the nitro-group is paralleled when these groups are attached to an aromatic ring and, by electron withdrawal, assist nucleophilic attack in the *para*-position. For example, the replacement of bromine in *p*-Br·C_6H_4·NO_2 by piperidine is some 32 times faster than in *p*-Br·C_6H_4·CN.[4] It would be unwise to place too much emphasis on this similarity since one cannot be certain that the ability of these groups to interact with the π-system of the benzene ring is in any way comparable with their ability to interact with the d_ϵ-orbitals of the cobalt(III) ion. Although there is no other information available about the role of these ligands in the reactions of d^6-systems, studies of the *trans*-effect in platinum(II) complexes (d^8) indicate that the *trans*-effect of the cyanide is greater than that of the nitro-ligand. It is now believed that this *trans*-effect arises mainly from the extent to which the ligand can assist bimolecular substitution of a labile ligand in the *trans*-position.[6]

TABLE 3.

Kinetic and steric course data for aquation and base hydrolysis of *trans*-[Co en_2 CN Cl]$^+$ and *trans*-[Co en_2 NO_2 Cl]$^+$.

Aquation.

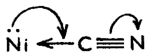
	k_1 (25°) (sec.$^{-1}$)	E_{act} (kcal./mole)	$\log_{10} A$	*cis*-Product (%)
CN	$8·2 \times 10^{-5}$	22·6	12·4	Small
NO_2	$9·8 \times 10^{-4}$ *	21·6 *	12·8 *	0 *

Base hydrolysis.

	k_2 (0°) (l. sec.$^{-1}$ mole^{-1})	E_{act} (kcal. mole)	$\log_{10} A$	*cis*-Product (%)
CN	0·13	23·2	17·7	Small
NO_2	0·080 *	24·4 ‡	18·4 ‡	6 *

* Data from ref. 1*a*. ‡ Data from ref. 5.

Other information of a non-kinetic character comes from the ability of these ligands to stabilise low oxidation states; for instance, complexes of the type $K_4[Ni(CN)_4]$ [7] and $K_4[Pd(CN)_4]$ [8] are well known in which the cyanide stabilises nickel (0) and palladium (0), presumably by withdrawing charge conjugatively from the metal (cf. A). This type of displacement is identical with that invoked for the labilising power of the nitro- and cyano-ligands in the aquation of the cobaltammine complexes, and yet complexes of the type $K_4[Ni(NO_2)_4]$, in which nickel (0) is stabilised by the nitro-group, are not known. Their absence may indicate that the nitro-group is less effective than cyanide when interacting with a nearly filled *d*-shell or may just reflect the lack of purposeful research in this direction. At this stage of the study there is insufficient information for us to be certain that there is a discrepancy in these various observations, let alone to try to resolve it.



(A)

Experimental.—The preparations and analyses of the compounds used in this investigation, *trans*-[Co en_2 CN Cl]NO_3, *trans*-[Co en_2 CN Cl]Cl,H_2O, *trans*-[Co en_2 CN OH]Cl,2H_2O and *trans*-[Co en_2 CN H_2O]$(ClO_4)_2$ are reported elsewhere, together with the evidence for the assignment of configuration.[3]

Kinetics. The aquation studies were carried out by the usual methods whereby a weighed quantity of the complex was dissolved in a known volume of water that had previously been brought to the reaction temperature, and samples were withdrawn by a pipette at the appropriate times. These were cooled rapidly and passed down an ice-jacketed column of Amberlite IR-120 cation-exchange resin in the acid form, and the effluent and the washings, which contained all the ionic chloride present in the reaction sample, were titrated with standard silver nitrate solution by Volhard's method. The resin column was flushed with water before each separation

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[4] Bunnett and Levitt, *J. Amer. Chem. Soc.*, 1948, **70**, 2778.

[5] Chan and Tobe, *J.*, 1962, 4531.

[6] (*a*) Chatt, Duncanson, and Venanzi, *J.*, 1955, 4456; (*b*) Basolo, Chatt, Gray, Pearson, and Shaw, *J.*, 1961, 2207.

[7] Eastes and Burgess, *J. Amer. Chem. Soc.*, 1942, **64**, 1187.

[8] Burbage and Fernelius, *J. Amer. Chem. Soc.*, 1943, **65**, 1484.

in order to remove any extra ionic chloride formed in the resin by the aquation of the absorbed chloro-complex. The studies of base hydrolysis were carried out with solutions of weighed amounts of complex in aqueous sodium hydroxide solution of the required concentration that had previously been brought to the reaction temperature. The reaction was stopped by running the samples into a slight excess of cooled nitric acid, and the ionic chloride was estimated as before. Thermostats were reliable to $\pm 0{\cdot}05°$ and light was excluded by the addition of Nigrosine Black dye to the thermostat-water.

Spectra were measured with a Unicam S.P. 500 Quartz Spectrophotometer.

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