522. *Preparation, Properties, and Reactions of a Bromocyano-bis(ethylenediamine)cobalt(III) Isomer.*

By S. C. CHAN.

Salts of a bromocyanobis(ethylenediamine)cobalt(III) cation have been prepared and characterised. The complex has been assigned a *trans*-configuration on the basis of infrared spectral and other observations. The kinetics of the aquation and base hydrolysis of the cation have been studied. The aquation is slower and the base hydrolysis somewhat faster than those of the corresponding bromonitro-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 known aquocyanobis(ethylene-diamine)cobalt(III) isomer. It is believed that all three reactions proceed with retention of configuration.

A NUMBER of cyanocobaltammine complexes have already been described, *e.g.*, aquo-cyanotetramminecobalt(III) chloride [1] and *cis*-dicyanobis(ethylenediamine)cobalt(III) salts.[2,3] Chan and Tobe [3] have described a series of salts of the complex cations $[Co\,en_2\,CN\,X]^{(2-m)+}$ (where $X = Cl^-$, OH^-, and H_2O, and m represents the number of negative charges on X) and studied their reactions.[4] These complexes have been assigned a *trans*-configuration, based on the absence of splitting of the ethylenediamine skeletal vibration at about 890 cm.$^{-1}$.[5] A non-ionic sulphitocyano-complex has also been described [3] but its configuration was uncertain, as a split peak does not necessarily indicate a *cis*-configuration. The preparation, properties, and reactions of the *trans*-bromocyanobis(ethylenediamine)-cobalt(III) complex are now reported.

(1) *Preparation, Properties, and Configuration of the Bromocyanobis(ethylenediamine)-cobalt(III) Complex.*—Direct reaction between dihalogenobis(ethylenediamine)cobalt(III) complexes and cyanide ion has been shown to take place, depending on conditions, in three ways,[3] none of which yields a halogenocyanobis(ethylenediamine)cobalt(III) complex, as expected to be formed by direct replacement of the co-ordinated halogen by cyanide. Thus, (*a*) with concentrated equimolar solutions of potassium cyanide and *trans*-dichloro-bis(ethylenediamine)cobalt(III) chloride, a disproportionation takes place, leading to the formation of tris(ethylenediamine)cobalt(III) chloride, together with some unidentifiable products which possess very unusual properties. (*b*) In dilute solutions and in the presence of small amounts of Co(II) species, a very rapid reaction takes place, forming a yellow orange solution containing pentacyanocobalt(III) species. In this case, a redox process is involved. (*c*) When carefully purified reagents are used, the only reaction observed is

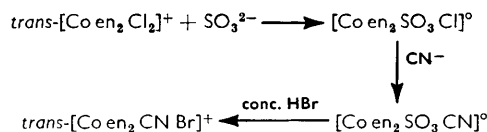[1] Hofmann and Reinsch, *Z. anorg. Chem.*, 1898, **16**, 377.
[2] Ray and Sarma, *J. Indian Chem. Soc.*, 1951, **28**, 59.
[3] Chan and Tobe, *J.*, 1963, 966.
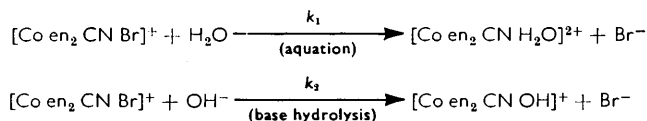[4] Chan and Tobe, *J.*, 1963, 541.
[5] Baldwin, *J.*, 1960, 4369.

hydroxide substitution by hydrolysis of the cyanide ion. The bromocyanobis(ethylene-diamine)cobalt(III) complex is now obtained *via* the sulphitocyano-complex by the following sequence of reactions:

$$\textit{trans-}[Co\ en_2\ Cl_2]^+ + SO_3{}^{2-} \longrightarrow [Co\ en_2\ SO_3\ Cl]^0$$

$$\downarrow CN^-$$

$$\textit{trans-}[Co\ en_2\ CN\ Br]^+ \xleftarrow{\text{conc. HBr}} [Co\ en_2\ SO_3\ CN]^0$$

The presence of the sulphito-group assists the entry of cyanide ion into the complex. The complex so obtained was in the form of the bromide, from which the nitrate could be obtained by the action of ammonium nitrate. The visible spectra of the bromide and the nitrate were found to be identical, showing that the complex cation was isomerically pure. The action of hydroxide ion on the bromocyano-complex followed by acidification of the product gives the isomer of the aquo-product that was also formed directly by the uncatalysed aquation or by Hg^{2+}-catalysed aquation. Spectrophotometrically, the product was identical to that obtained similarly from the chlorocyano-complex.[4] The spectra of both the bromocyanobis(ethylenediamine)cobalt(III) complex and the aquo-product are given in the Figure. The assignment of a *trans*-configuration to the complex is based on the following evidence: (*a*) The infrared absorption peak at about 890 cm.$^{-1}$, assigned to the skeletal vibration of the ethylenediamine, is not split. This test has been applied successfully to many $[Co\ en_2\ XY]^{n+}$ complexes of known configuration. (*b*) A crystalline salt $[Co\ en_2\ CN\ Br]Z$ where Z is the $(+)$-α-bromo-π-camphorsulphonate ion, a very effective resolving agent for *cis*-bis(ethylenediamine)cobalt(III) complexes, but neither fractional crystallisation nor fractional precipitation gave a sample that had optical activity assignable to the cation. It must be admitted, however, that the above evidence, although reasonable, is not yet conclusive.

(2) *Reactions of* trans-*Bromocyanobis(ethylenediamine)cobalt*(III) *Cation.*—The kinetics of both these reactions were followed by studying the increase of the concentration of free bromide ion in the solution titrimetrically. The anionic bromide was separated from the complex cation by means of a cation-exchange resin and was determined with standard silver nitrate solution. The first-order rate constants for aquation, k_1, were determined from the slopes of the plots 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 co-ordinated bromide. Titration of the reaction mixture after ten half-lives indicated that, even when the complex was supplied as the bromide, equilibrium was reached with 97% aquation. The base hydrolysis was relatively rapid, and followed

$$[Co\ en_2\ CN\ Br]^+ + H_2O \xrightarrow[\text{(aquation)}]{k_1} [Co\ en_2\ CN\ H_2O]^{2+} + Br^-$$

$$[Co\ en_2\ CN\ Br]^+ + OH^- \xrightarrow[\text{(base hydrolysis)}]{k_2} [Co\ en_2\ CN\ OH]^+ + Br^-$$

a simple second-order rate law, $d[Br^-]/dt = k_2[\text{complex}][OH^-]$, in which complications caused by the replacement of co-ordinated cyanide are absent, and those induced by simultaneous background aquation are negligible. The reaction was followed by a sampling method, whereby portions of the reaction mixture were withdrawn and delivered into vessels containing excess of cooled dilute nitric acid. The techniques used to initiate the reaction and sample the mixture depended upon the rate. For relatively slow reactions, the reagents were mixed in a flask and samples were withdrawn at suitable times by pipette. Fast reactions were followed with an apparatus where the reagents were mixed in a three-way tap and reacted while passing along a tube. The reaction was stopped almost instantaneously when the solution emerged and ran into excess of acid. The ionic

bromide was then determined as described above. The second-order rate constants, k_2, were calculated by one of the following integrated expressions, depending on circumstances:

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

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

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

In the above expressions, 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 bromide ion between times $t = 0$ and t. The rate constants of both reactions, given in Table 1, have the following temperature dependence:

$$k_1 = 1 \cdot 6 \times 10^{14} \exp(-24{,}000/\boldsymbol{R}T) \text{ sec.}^{-1}$$
$$k_2 = 7 \cdot 9 \times 10^{18} \exp(-23{,}400/\boldsymbol{R}T) \text{ l. sec.}^{-1} \text{ mole}^{-1}.$$
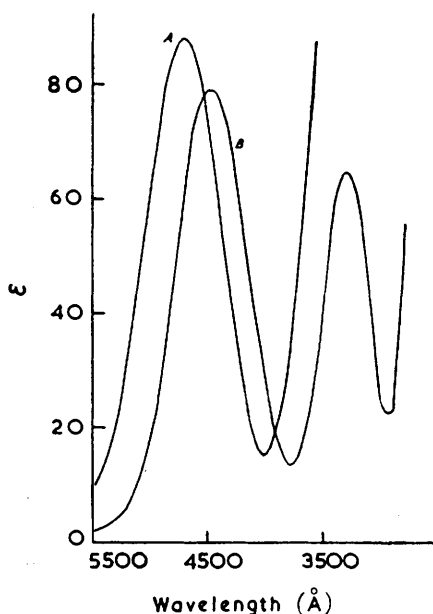
Absorption spectra of (*A*) *trans*-bromocyanobis-(ethylenediamine)cobalt(III) cation and (*B*) its aquation product.

Since only one isomer of the aquocyano-product has been isolated, the steric courses of the aquation and the base hydrolysis cannot be determined with certainty. However, the products of the three reactions, (*a*) aquation, (*b*) mercuric ion-catalysed aquation, and (*c*) base hydrolysis of *trans*-bromocyanobis(ethylenediamine)cobalt(III) cation were examined spectrophotometrically. Three solutions of the complex 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 reaction was complete. The spectra of these three solutions were virtually identical with the spectrum of a pure sample of *trans*-aquocyanobis(ethylenediamine)-cobalt(III) cation (see Figure). Mercuric ion-catalysed aquations have been observed in the past to take place with complete retention of configuration, even in complexes where direct aquation in the absence of mecuric ions may lead to considerable steric change.[6] It can

[6] Staples and Tobe, *J.*, 1960, 4812.

TABLE 1.

Rate constants for aquation and base hydrolysis of *trans*-bromocyanobis(ethylene-diamine)cobalt(III) bromide in aqueous solutions.

Aquation

Temp.	Initial [complex] (mmole/l.)	$10^5 k_1$ (sec.$^{-1}$)	Temp.	Initial [complex] (mmole/l.)	$10^5 k_1$ (sec.$^{-1}$)	Temp.	Initial [complex] (mmole/l.)	$10^5 k_1$ (sec.$^{-1}$)
0·0°	4·08	1·19	10·2°	4·00	5·42	25·1°	4·03	48·0
,,	5·02	1·12	,,	5·05	5·70	,,	5·03	46·1
,,	6·07	1·13	,,	6·04	5·42	,,	6·04	46·6
,,	7·08	1·18	,,	7·04	5·58	,,	7·04	46·6

Base hydrolysis

Temp.	Initial [complex] (mmole/l.)	Initial [OH$^-$] (mmole/l.)	k_2 (l.sec.$^{-1}$ mole^{-1})	Temp.	Initial [complex] (mmole/l.)	Initial [OH$^-$] (mmole/l.)	k_2 (l.sec.$^{-1}$ mole^{-1})
0·0°	1·02	10·0	1·89	25·1°	1·00	4·00	68·8
,,	2·09	,,	1·75	,,	2·04	5·00	65·4
,,	3·07	,,	1·81	,,	3·04	6·00	66·1
,,	4·04	,,	1·75	,,	4·05	4·05	68·1
,,	3·05	7·0	1·81				
10·2	1·01	10·0	8·34				
,,	2·03	,,	8·52				
,,	3·00	,,	8·68				
,,	4·06	,,	8·77				

thus be concluded that, unless the spectra of the two isomers of the product are virtually identical, all three reactions proceed with almost complete retention of configuration, within the limits of reliability of the assignment of configuration to the complexes used.

DISCUSSION

The foregoing results are collected in Table 2 where they are compared with the corresponding values for similarly related complexes.

TABLE 2.

Kinetic and steric course data for aquation and base hydrolysis of some *trans*-halogenocyano- and *trans*-halogenonitro-bis(ethylenediamine)cobalt(III) cations.

$$k = B \exp(-E/RT)$$

Aquation

Orienting group	Replaced group	k_1 (0°) (sec.$^{-1}$)	E (kcal./mole)	$\log_{10} B$	*cis*-Product (%)
CN	Br	$1·2 \times 10^{-5}$	24·0	14·2	Small
NO$_2$	Br	$1·4 \times 10^{-4}$ *	23·1 *	14·6 *	—
CN	Cl	$2·3 \times 10^{-6}$ †	22·6 †	12·4 †	Small †

Base hydrolysis

Orienting group	Replaced group	k_2 (0°) (l.sec.$^{-1}$ mole^{-1})	E (kcal./mole)	$\log_{10} B$	*cis*-Product (%)
CN	Br	1·80	23·4	18·9	Small
NO$_2$	Br	0·68 ‡	—	—	—
CN	Cl	0·13 †	23·2 †	17·7 †	Small †

* Data from ref. 7.   † Data from ref. 4.   ‡ Data from a single determination.   The very slight effect of background aquation was neglected.

These results may be discussed under two different headings: (a) Labilising effect of the cyano-group compared with that of the nitro-group, and (b) effect of the displaced group on the rates find Arrhenius parameters.

Chan and Tobe [4] have observed that the rate of aquation of *trans*-chlorocyanobis(ethylenediamine)cobalt(III) cation is some 12 times slower than that of the chloronitro-complex.

[7] Langford and Tobe, *J.*, 1963, 506.

These results find their counterpart in the aromatic systems, *e.g.*, the replacement of bromine in p-Br·C_6H_4·CN by piperidine is some **32** times slower than in p-Br·C_6H_4·NO_2.[8] The results in Table 2 show that the aquation of *trans*-bromocyanobis(ethylenediamine)-cobalt(III) cation is also about 12 times slower than that of the bromonitro-complex. This lesser labilising power of the cyano-group compared with that of the nitro-group is due to its smaller electronegative conjugative effect $(-T)$ which can retract part of the cobalt $3d_\epsilon$ shell. Since this effect facilitates S_N2 and inhibit S_N1 aquations, the aquation data are consistent with a bimolecular mechanism. On the other hand, the base hydrolysis of both chloro- and bromocyano-complexes are 2—3 times faster than those of the corresponding nitro-complexes. This is not surprising since both the S_N2 and the S-$1cb$ mechanisms, which are hitherto used to explain the base hydrolysis of halogenobis(ethylene-diamine)cobalt(III) cations, require that the electron-displacing properties of the orienting group have no large effect on the rate of the reaction. In a bimolecular process in which bond-making and -breaking are of roughly equal importance, the electron displacements which assist the former hinder the latter, and *vice versa*. Similarly, in the S_N1cb mechanism, electron withdrawal increases the concentration of conjugate base in equilibrium with a given amount of base, but, at the same time, decreases the lability of the outgoing group. The small increase in the rate of base hydrolysis when the orienting group is changed from nitro to cyano is consistent with Chan and Tobe's mechanism[9] which also involves a bimolecular reaction between the hydroxide ion and the complex, but the way in which the reagents come together are of prime importance. Thus the rates and steric courses of the reaction will depend on two probability functions: (*a*) The probability of finding the hydroxide ion in a particular position, and (*b*) the probability that an attack from the point in question results in replacement. The probabilities of finding the hydroxide ion near the nitro- and the cyano-ligands, respectively, are high, but the reaction from this position is hindered by the polarisation of the cobalt caused by the $-T$ effect. Major attack will therefore take place adjacent to the outgoing halogen, thus explaining the almost complete retention of configuration in both cases. The same polarisation of cobalt will oppose heterolysis of the departing halogen, and thus a balance of opposing effects is set up, the rates of reaction then depending on whether the importation of electrons by the incoming hydroxide requires only a smaller, or a larger, simultaneous release of electrons towards the outgoing halogen to produce the transition state. Asperger and Ingold[10] suggested that in the base hydrolysis of chloronitrobis(ethylenediamine)cobalt(III) cations, the electron release is slightly the more important of the two process of electron transfer involved, and our data on the base hydrolysis of the halogenocyanobis(ethylenediamine)-cobalt(III) complexes support their suggestions since the lesser polarising effect of the cyano-group will retard the heterolysis of the departing halogen to a smaller extent than does the nitro-group, thus leading to a slightly greater reaction rate.

Secondly, in the aquation of *trans*-[Co en$_2$ CN X]$^+$, a change from X = Cl to X = Br increases both the rate of aquation and the activation energy. This supports the existing mechanism[11] in which hydrogen bonding between the incoming water and the outgoing halogen, in the order Cl > Br, lowers the activation energy.

<center>EXPERIMENTAL</center>

Preparations.—trans-*Bromocyanobis(ethylenediamine)cobalt*(III) *bromide* was prepared by the action of concentrated hydrobromic acid on the cyanosulphito-complex.[3] The crystalline salt was filtered off, washed with alcohol and ether, and dried. No further recrystallisations were necessary {Found: Co, 16·0; co-ordinated Br, 21·7; Br⁻, 22·0. [Co en$_2$ CN Br]Br requires Co, 16·1; co-ordinated Br, 21·9; Br⁻, 21·9%}; $\nu_{max.}$ 2137 cm.⁻¹ (C–N stretch), 885 cm.⁻¹ (CH$_2$ rock).

[8] Bunnett and Levitt, *J. Amer. Chem. Soc.*, 1948, **70**, 2778.
[9] Chan and Tobe, *J.*, 1962, 4531.
[10] Asperger and Ingold, *J.*, 1956, 2862.
[11] Tobe, *J.*, 1959, 3776.

trans-*Bromocyanobis(ethylenediamine)cobalt*(III) *nitrate* was prepared from the bromide by the action of ammonium nitrate. The crystals were filtered off, washed with alcohol and ether, and dried. {Found: Co, 16·7; co-ordinated Br, 22·8; Br⁻, absent. [Co en₂ CN Br]NO₃ requires Co, 17·0; co-ordinated Br, 23·0%}.

trans-*Bromocyanobis(ethylenediamine)cobalt*(III) (+)-α-*bromocamphor-π-sulphonate* was prepared by mixing an aqueous solution of the complex bromide with small portions of solid ammonium (+)-α-bromocamphor-π-sulphonate. The crystals were filtered off in batches as they were formed, washed with alcohol and ether, and dried. There was no indication of optical activity that did not come from the resolving agent {Found: Co, 9·9.   [Co en₂ CN Br]C₁₀H₁₄BrO₄S requires Co, 9·9%}.

trans-Aquocyanobis(ethylenediamine)cobalt(III)   nitrate was prepared from the *trans*-chlorocyano-chloride by the method of Chan and Tobe.[3]   The complex was purified by adding alcohol to its aqueous solution twice {Found: Co, 16·9.   Calc. for [Co en₂ CN H₂O](NO₃)₂: Co, 17·0%}.

trans-Bromonitrobis(ethylenediamine)cobalt(III) bromide was prepared by the method of Langford and Tobe.[7]   The crude product was refluxed with an alcoholic solution of anisole and recrystallised by grinding it with portions of bromine-free 45% hydrobromic acid, adding an equal volume of alcohol to the filtrate, and cooling in ice {Found: Co, 15·1; co-ordinated Br, 20·7; Br⁻, 20·7.   Calc. for [Co en₂ NO₂ Br]Br: Co, 15·3; co-ordinated Br, 20·7; Br⁻, 20·7%}.

Kinetics.—At 0°, the thermostat was a large Dewar flask filled with crushed ice and water. Other thermostats were of the conventional design capable of holding temperatures constant to ± 0·05°.   Light was carefully excluded during the reaction.

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 passed down an ice-jacketed column of Amberlite IR-120 cation-exchange resin in the acid form, and the effluent and washings, which contained all the ionic bromide present in the reaction sample, were titrated with standard silver nitrate solution.   The resin column was flushed with water before each separation in order to remove any extra bromide ion formed in the resin by the aquation of the absorbed bromo-complex.

The studies of base hydrolysis were carried out with solutions of the necessary amounts of sodium hydroxide and the complex, both of which had previously been brought to reaction temperatures.   The reagents were then mixed at zero time.   At 0°, timed samples were withdrawn with a jacketed fast-running pipette and delivered into cooled vessels containing an excess of nitric acid.   At higher temperatures, a fast reaction apparatus similar to that described by Chan and Tobe [9] was used.   This consisted of two thermostat-controlled reservoirs which could be connected, by turning a three-way tap, to a thermostat-controlled reaction tube. Equal volumes of solutions of complex and alkali were placed in the reservoirs and when thermal equilibrium was reached, the tap was opened and the solution forced by compressed air into the reaction tube.   Mixing was shown to be complete within the tap, and the reagents reacted while passing along the tube.   On emerging from the other end, they were run into an excess of cooled nitric acid and the ionic bromide in the solution was estimated as before.   The calibrations and detailed procedures of the apparatus were described by Chan and Tobe.[9]

Measurements.—Visible absorption spectra were measured with a Unicam S.P. 500 quartz spectrophotometer and 4-cm. silica cells.   Infrared measurements were made with a Perkin-Elmer Infracord model 137 spectrometer on the solid complex, which was ground to a mull with Nujol and placed between potassium bromide or sodium chloride plates.   Polarimetric measurements were made visually with a Hilger and Watts Mark III polarimeter and a sodium lamp.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF HONG KONG,
    HONG KONG.   [*Received, September* 10*th,* 1963.]