178. *Preparation and Properties of Cyanobisethylenediaminecobalt*(III) *Complexes, and the Role of Cyanide as a Substituting Agent.*

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The reaction between *trans*-$[Co\,en_2Cl_2]^+$ and cyanide ion in concentrated and dilute solution has been studied. In concentrated solution, with equimolar quantities, there is a disproportionation to form $[Co\,en_3]^{3+}$ and some unidentifiable products which possess very unusual properties. In dilute solution, with carefully purified reagents, the only reaction observed is hydroxide substitution by hydrolysis of the cyanide ion. It has been conclusively shown that cyanide is effective as a reagent only when cobalt(II) species are present to act as catalysts, the mechanism being a redox process. Salts of the following cations $[Co\,en_2(CN)_2]^+$, $[Co\,en_2(CN)Cl]^+$, $[Co\,en_2(CN)OH]^+$, and $[Co\,en_2(CN)H_2O]^{2+}$ have been prepared by more complicated reactions. The dicyano-complex, previously assigned the *trans*-configuration, has been resolved and so is the *cis*-isomer. It was not possible to obtain more than one isomeric form of any of these complex cations. All the monocyano-complexes have been assigned a *trans*-configuration on the basis of infrared and other observations. The racemisation of *cis*-$[Co\,en_2(CN)_2]^+$ is very slow but takes place without noticeable decomposition. In all these complexes the cyanide is bound very strongly to the cobalt and is unaffected by prolonged heating with acid or base.

FOR studies of the reaction mechanisms of cobalt(III) complexes information is required about the behaviour of, as yet, unexamined ligands. The cyanide group is in this respect of three-fold interest. First, as a non-participating ligand, by virtue of its high polarisability, it forms a strong σ-bond and is believed also to accept back-donation from metals in complexes involving their low oxidation states, *e.g.*, in $K_4[Ni(CN)_4]$.[1] The effect of the cyanide ligand on the displacement of co-ordinated chlorine in aquation and base-hydrolysis is reported in another paper.[2] Secondly, it has been claimed that the cyanide ion is a better nucleophile than hydroxide ion towards cobalt(III) [3] and, if this could be substantiated, it was thought that a study of cyanide substitution might provide an unambiguous example of a bimolecular substitution in a cobalt(III) complex. Thirdly, the lability or inertness of the cobalt–cyanide bond is of interest. Independent preparation and characterisation of relevant cyanide-containing complexes constitutes the first step of this study.

The complex,[4] $[Co(NH_3)_4(H_2O)CN]Cl_2$, which was said to be produced from the cyanide, $[Co(NH_3)_4(H_2O)SO_3]CN$, by concentrated hydrochloric acid remained for fifty years the only known monocyanocobaltammine. Recently, $[Co\ en_2(CN)_2]^+$ salts were obtained by the action of potassium cyanide on the salts *cis*- and *trans*-$[Co\ en_2(S_2O_3)_2]Na$ and were consequently assigned a *trans*-configuration.[5] We now assign a *cis*-configuration to this complex and also describe a series of monocyanobis(ethylenediamine)cobalt(III) complexes. The mechanism of the fast reaction between *trans*-$[Co\ en_2Cl_2]^+$ and potassium cyanide has been studied and the lability of co-ordinated cyanide has also been investigated.

Reaction between trans-*Dichlorobisethylenediaminecobalt*(III) *Chloride and Potassium Cyanide.*—When concentrated solutions of equimolecular amounts of potassium cyanide and the salt *trans*-$[Co\ en_2Cl_2]Cl$ were mixed, heat was evolved and the solution, on cooling, deposited the orange-yellow trichloride $[Co\ en_3]Cl_3$. An orange-red complex was precipitated as an oil or a deliquescent powder on addition of alcohol to the filtrate. If the cyanide solution was added drop by drop to a cooled and stirred solution of the *trans*-dichloro-chloride the colour changed to orange-red but no trisethylenediaminecobalt(III) trichloride was formed, but the orange-red complex was obtained as previously. This compound could not be obtained crystalline but analysis indicated an approximate composition, $Co\ en_2(CN)Cl_2,2H_2O$. The complex was very soluble in water and a dilute aqueous solution passed through a mixed-bed ion-exchange resin without change in the absorption spectrum. The solution, nevertheless, had the electrical conductivity expected for a 1 : 1 electrolyte (calculated on the basis of one cobalt atom per complex ion), and this conductivity was unchanged on passage through this mixed-bed resin. A more concentrated aqueous solution had the light-scattering properties of a colloidal solution and addition of dilute perchloric acid or sodium perchlorate precipitated an oil or an orange powder which, although insoluble in this medium, was deliquescent after filtration and washing with alcohol and ether. This precipitation phenomenon was found for many, but by no means all, electrolytes. For example, hydrochloric acid did not produce a precipitate. The complex is probably polymeric, but its peculiar properties cannot yet be explained.

Preliminary studies of the reaction between *trans*-$[Co\ en_2Cl_2]^+$ and cyanide in dilute solution suggested a very rapid reaction, forming a yellow-orange solution, and it was thought at first that this was further indication of the rapid reaction between cobaltammine complexes and cyanide ions reported by other workers.[3a] However, when purified reagents were used this colour change could not be reproduced and, instead, a violet solution was produced, whose colour changed to green on acidification. The kinetics of the reaction were studied spectrophotometrically (6200 Å) with the presence of sufficient cyanide to ensure pseudo-first-order kinetics. The rate constants were determined from

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

[2] Chan and Tobe, *J.*, 1963, 514.

[3] (*a*) Nagarajaiah, Sharp, and Wakefield, *Proc. Chem. Soc.*, 1959, 385; (*b*) Hope and Prue, *J.*, 1960, 2782.

[4] Hoffmann and Reinsch, *Z. anorg. Chem.*, 1898, **16**, 377.

[5] Ray and Sarma, *J. Indian Chem. Soc.*, 1951, **28**, 59.

the slope of the semilogarithmic plot of $\log_{10} (D_t - D_\infty)$ against time, t, where D_t and D_∞ are the optical densities of the solutions acidified at time, t, and after 10 half-lives, respectively. k_1 was found to have a half-order dependence upon the total concentration of potassium cyanide (Fig. 1). This is the kinetic form for a reaction whose rate is proportional to the concentration of hydroxide ions produced by hydrolysis of cyanide:

$$CN^- + H_2O \overset{K_{hyd}}{\rightleftharpoons} HCN + OH^-$$

For this equilibrium, $K_{hyd} = [OH^-][HCN]/[CN^-]$ and, since we are dealing with solutions of KCN in water, $[OH^-] = [HCN]$. Balancing the cyanide containing species, we have $[KCN] = [HCN] + [CN^-]$, and substituting for [HCN] and $[CN^-]$ in this we get

$$[OH^-] + [OH^-]^2/K_{hyd} = [KCN],$$

from which we find that

$$[OH^-] = \{-K_{hyd} + (K^2_{hyd} + 4K_{hyd}[KCN])^{\frac{1}{2}}\}/2.$$

Now, K_{hyd} (see below) is sufficiently small compared with [KCN] for this expression to simplify to $[OH^-] = K^{\frac{1}{2}}_{hyd}[KCN]^{\frac{1}{2}}$ in the concentration range $10^{-2}M < [KCN] < 10^{-1}M$.

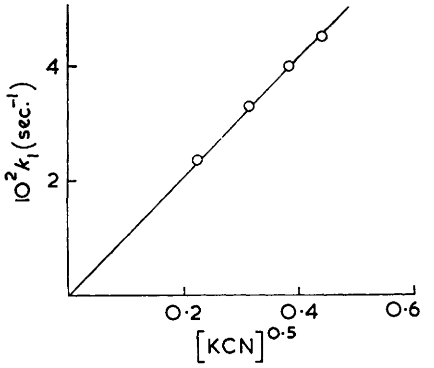

FIG. 1. The reaction between KCN and *trans*-$[Co\ en_2Cl_2]^+$: pseudo-first-order rate constant, k_1, plotted against $[KCN]^{0·5}$.

It is possible to use the slope of the half-order cyanide plot to obtain a second-order rate constant for the hydroxide-dependent reaction. If the kinetic form of the reaction is Rate $= k_2[OH^-][Complex]$, the slope of the plot of k_1 against $[KCN]^{\frac{1}{2}}$ is equal to $k_2(K_{hyd})^{\frac{1}{2}}$.

An accurate value for K_{hyd} of the cyanide ion at 0·8° is not available, but $K_{hyd} = K_w/K_A$, where $K_w = 1·14 \times 10^{-15}M^2$ at 0·0°.[6] Here, $K_A = [H^+][CN^-]/[HCN]$, but is not known at 0°. However, since this constant appears not to vary greatly with temperature, we have used the value at 25° ($7·2 \times 10^{-10}M$).[7] In this way a value for k_2, = 81 l. sec.$^{-1}$ mole^{-1} at 0·8° was obtained and this compares well with the value determined by direct study[8] of the reaction in the absence of cyanide ions (95 l. sec.$^{-1}$ mole^{-1}) in view of the inaccuracies involved. This agreement indicates (*a*) that the value assumed for K_A is reasonable and (*b*) that the reagent is the hydroxide ion. The latter point was confirmed on finding that the spectrum of a solution that had been acidified after about ten half-lives of the reaction corresponded almost exactly to that of a 19 : 1 mixture of *trans*- and *cis*-$[Co\ en_2(H_2O)Cl]^{++}$, which is the isomeric ratio of the products of hydroxide substitution carried out in the absence of cyanide.[8] It is clear then that the reaction is not cyanide substitution and that cyanide does not enter the complex at any stage of the reaction. When acid was added to suppress the formation of hydroxide ions the reaction was stopped

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[6] Harned and Owen, " Physical Chemistry of Electrolytic Solutions," Second Edition, Reinhold, New York, 1950, p. 485.

[7] Lange, " Handbook of Chemistry," 10th edn., McGraw-Hill, New York, 1961, p. 1200.

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

completely. The preliminary observations that indicated a different reaction leading to the formation of cyanide-containing species still required explanation, and experiments were carried out in which small quantities of cobaltous chloride solution were added to the solution of the complex *trans*-$[Co\,en_2Cl_2]Cl$ before addition of cyanide. The colour change, green to yellow, was again observed; the spectra of these solutions, measured after acidification, when the reaction was complete, are given in Fig. 2. In the absence of cobalt(II) species, the spectrum is that of the mixture of the two aquochloro-isomers already discussed but, in the presence of cobalt(II), a new species appears to be formed in competition with hydroxide substitution; its formation is catalysed by cobalt(II), one molar part of which to ten of complex yields about 85% of the new product. The spectrum of the yellow solution did not appear to correspond to that of any known cyanobisethylenediaminecobalt(III) complexes but there was a general similarity to the spectra of complexes of the type $[Co(CN)_5X]^{n-}$,[9] although absorption was too high in the region 2800—3400 Å. The experiments were repeated in the absence of dissolved or atmospheric oxygen; the spectra were then considerably modified in this region, which is shown in Fig. 3. The different spectrum obtained when the dibromo-bromide *trans*-$[Co\,en_2Br_2]Br$ was used indicates strongly that this cobalt(II)-catalysed reaction has a mechanism of the type put forward by Adamson [10] to explain the reaction between halogenopentamminecobalt(III) complexes and cyanide, *i.e.*:

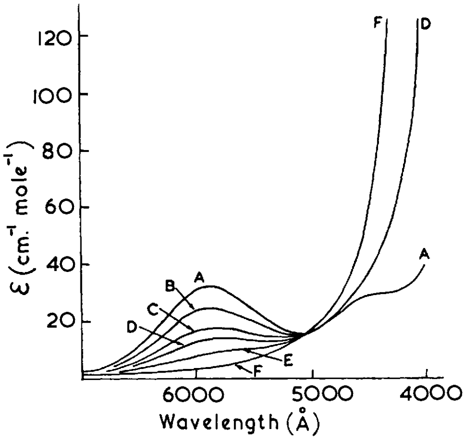

FIG. 2. Spectra of acidified products of the reaction between *trans*-$[Co\,en_2Cl_2]^+$ and an excess of KCN, in the presence of $CoCl_2$.

[Complex] = 4×10^{-3}M. $[Co^{2+}]$ = (A) 0, (B) 5×10^{-5}, (C) 1×10^{-4}, (D) 2×10^{-4}, (E) 4×10^{-4}, (F) 6×10^{-4}M.

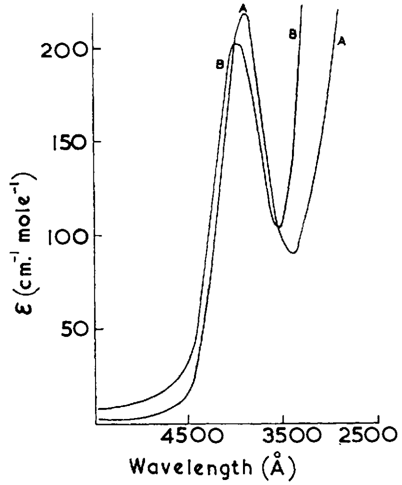

FIG. 3. Spectra of acidified reaction products of the reaction between an excess of KCN and (A) *trans*-$[Co\,en_2Cl_2]^+$ and (B) *trans*-$[Co\,en_2Br_2]^+$ in the absence of oxygen and the presence of sufficient Co(II) catalyst.

$$Co^{2+} + 5CN^- \rightleftharpoons [Co(CN)_5]^{3-}$$

$$\begin{tikzcd} {[Co(CN)_5]^{3-} + [Co\,en_2Cl_2]^+} \arrow[r] & {[(CN)_5Co{-}Cl{-}Co\,en_2Cl]^{2-}} \arrow[d] \\ & {[(CN)_5CoCl]^{3-} + Co^{2+} + 2en + Cl^-} \end{tikzcd}$$

However, this does not account for all the material consumed under the conditions of our reaction.

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[9] Haim and Wilmarth, *J. Amer. Chem. Soc.*, 1961, **83**, 509.

[10] Adamson, *J. Amer. Chem. Soc.*, 1956, **78**, 4260.

It is concluded, therefore, that the reaction between *trans*-$[Co\ en_2Cl_2]^+$ and cyanide ions is not a nucleophilic substitution but is a redox-catalysed process in which the displacement of the ligands takes place when the metal is in its labile lower oxidation state. In dilute solution, where there was a large excess of cyanide, the product was of the type $[Co(CN)_5X]^{n-}$, where X either arises by bridge transfer from the original cobalt(III) complex or is one of the groups that can be attached when $[Co(CN)_5]^{3-}$ is oxidised in aqueous solution. In the preparative-scale experiments in concentrated solution conditions are such that $[CN^-] \leqslant$ [Complex], and the ratios [Co(II)] : [en] : $[CN^-]$ change as the reaction proceeds. In these conditions, the $[Co(CN)_5]^{3-}$ anion will no longer necessarily be the only reducing agent present and may be accompanied by any number of (unidentified) cobalt(II) complexes containing ethylenediamine and possibly even chloride in addition to cyanide. The oxidation of these by the *trans*-$[Co\ en_2Cl_2]^+$ cation can lead to formation of $[Co\ en_3]^{3+}$ as well as unidentified products.

TABLE 1.

Characteristic absorption frequencies (cm.$^{-1}$) of the infrared spectra of some mono- and di-cyanobisethylenediaminecobalt(III) complexes.

	Assignment			Assignment	
Complex	C–N stretch	CH_2 rock	Complex	C–N stretch	CH_2 rock
cis-$[Co\ en_2(CN)_2]Cl$	2137, 2128	894, 880	*trans*-$[Co\ en_2(CN)Cl]NO_2$	2137	888
$[Co\ en_2(CN)SO_3]$	2119	892, 886	*trans*-$[Co\ en_2(CN)H_2O](NO_3)_2$	2146	885
trans-$[Co\ en_2(CN)Cl]Cl,H_2O$	2132	889	*trans*-$[Co\ en_2(CN)OH]Cl,2H_2O$	2128	891

TABLE 2.

Racemisation of (+)-*cis*-dicyanobisethylenediaminecobalt(III) chloride in water at 80° (3·16 g./100 ml.; $l = 10$ cm.).

Time (hr.)	0	2	6	20	48	168
α	0·78	0·74	0·68	0·48	0·28	0·00
$\log_{10} (\alpha_0/\alpha)$	—	0·023	0·059	0·211	0·445	—
$k_{rac.}$ (hr.$^{-1}$)	—	0·026	0·023	0·024	0·024	—

Resolution and Racemisation of the cis-*Dicyanobisethylenediaminecobalt*(III) *Cation.*—Ray and Sarma [5] described the preparation of salts of the complex cation, $[Co\ en_2(CN)_2]^+$. Only one isomer could be obtained and this was assigned a *trans*-configuration because the same isomer was obtained irrespective of whether the starting compound was *cis*- or *trans*-$[Co\ en_2(S_2O_3)_2]^-$. However, in the infrared spectrum of the dicyano-chloride the peak assigned to the C–N stretch was split (Table 1), as was that at 880—890 cm.$^{-1}$. Both splittings indicate a *cis*-configuration; splitting of the C–N stretching frequency arises from the infrared activity of both the in-phase and the out-of-phase coupling of the *cis*-groups,[11] and splitting of the skeletal CH_2 rocking frequency of the ethylenediamine reflects the lower symmetry of the *cis*-isomer.[12] We then resolved the complex, as (+)-α-bromocamphor-π-sulphonate, confirming the assignment of the *cis*-configuration.

The *cis*-$[Co\ en_2(CN)_2]^+$ cation is extremely stable in both acid and alkaline solution. The absorption spectrum of a solution of the chloride in 0·1N-sodium hydroxide remained unchanged for 3 days at 80° and only slight decomposition was observed after 5 days. Similarly, in 0·1N-hydrochloric acid there was no change after 5 days at 80° and only slight decomposition after 7 days. An aqueous solution of the chloride (+)-*cis*-$[Co\ en_2(CN)_2]Cl$ was kept at 80° and the optical rotation at the Na_D line was measured from time to time on cooled samples. The data are collected in Table 2, where it can be seen that the racemisation has a half-life of about 29 hours and that the first-order rate constant for racemisation, $k_{rac.}$, is 0·024 hr.$^{-1}$ at 80°. It is of interest that the spectrum of

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[11] Chatt, Duncanson, Gatehouse, Lewis, Nyholm, Tobe, Todd, and Venanzi, *J.*, **1959**, 4073.

[12] Baldwin, *J.*, **1960**, 4369.

the solution which has lost all its optical activity is the same as that of a freshly prepared one, indicating racemisation and absence of decomposition. Further investigation is necessary before the mechanism can be discussed in detail.

Preparation, Properties, and Configurations of Other Monocyanobisethylenediamine-cobalt(III) *Complexes*.—The failure of the experiments designed to replace the co-ordinated chlorine in the dichlorobisethylenediaminecobalt(III) complexes by cyanide lead to a search for other methods of obtaining these complexes. For some undiscovered reason, the presence of a sulphite or a thiosulphate in the complex assists the entry of cyanide in conditions where little disproportionation takes place. The monocyano-complexes were obtained by the following sequence of reactions:

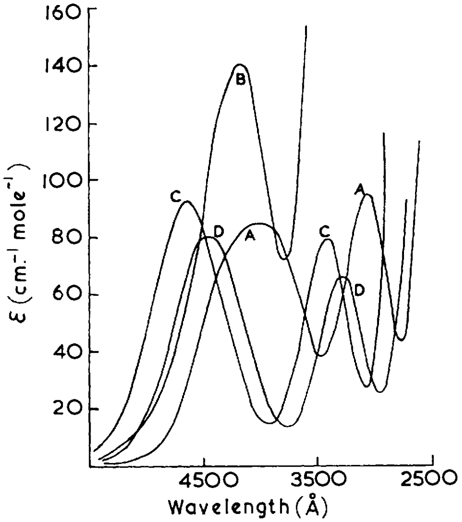


FIG. 4. Absorption spectra of some cyanobisethylenediaminecobalt(III) complexes.

(A) *cis*-[Co $en_2(CN)_2]_2S_2O_3,H_2O$.
(B) [Co $en_2(SO_3)CN$].
(C) *trans*-[Co $en_2(CN)Cl]Cl,H_2O$.
(D) *trans*-[Co $en_2(CN)H_2O](ClO_4)_2$.

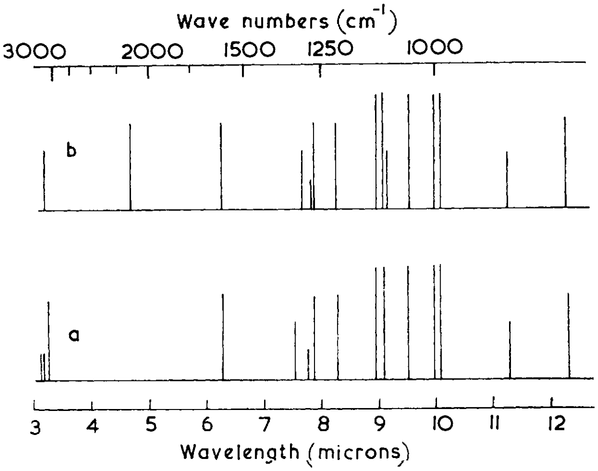
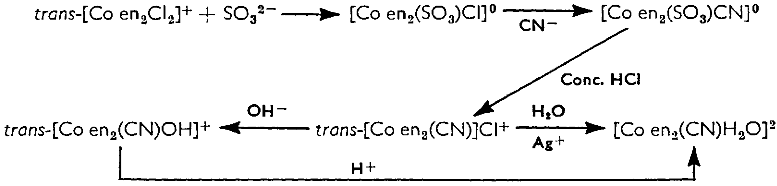


FIG. 5. Schematic comparison of the infrared absorption spectra of (a) *trans*-[Co $en_2Cl_2]Cl$ and (b) *trans*-[Co $en_2(CN)Cl]Cl$ in the frequency range 800—3000 cm.$^{-1}$.



In every case, only one isomer of the complex was obtained. The action of hydroxide on the chlorocyano-complex, followed by acidification of the product, gives the isomer of the aquo-complex that was also formed directly by uncatalysed aquation or by Ag^+- or Hg^{2+}-catalysed aquation. Replacement of the co-ordinated water by chloride regenerates the original chloro-complex without isomerisation. This uniform retention of configuration during substitution and the failure of the other attempts to introduce cyanide into the complex are the reasons for our inability to isolate the other isomers. A number of salts of the chlorocyano-cation were prepared and purified, and their visible absorption spectra were measured and found to be identical. This is added proof of the isomeric purity of these complexes. The spectra of the different cyano-complexes described in this paper are given in Fig. 4.

An attempt has been made to assign configurations to the monocyano-complexes that have been isolated, on the basis of the following evidence: (*a*) The infrared absorption peak at 890 cm.$^{-1}$, assigned to the skeletal vibration of the ethylenediamine, is not split and the infrared spectrum of the salt [Co en$_2$(CN)Cl]Cl is identical with that of *trans*-[Co en$_2$Cl$_2$]Cl in the range 800—3000 cm.$^{-1}$, except for the absorption at 2132 cm.$^{-1}$ which is assigned to the C–N stretch (Fig. 5). Relevant results are collected in Table 1. (*b*) A crystalline salt [Co en$_2$(CN)Cl]X was obtained where X is the (+)-α-bromo-π-camphorsulphonate ion, a very effective resolving agent for *cis*-bisethylenediaminecobalt(III) complexes, but neither fractional crystallisation nor fractional precipitation gave a sample that had optical activity assignable to the cation.

The splitting of the ethylenediamine skeletal vibration at 890 cm.$^{-1}$ has been thought to arise either from the lower symmetry of the *cis*-isomers [Co en$_2$XY]$^{n+}$, or from reduction of symmetry arising from N–H $\cdots$ Z$^-$ interactions between the amine protons and the anions in the crystal lattice.[12] The absence of splitting of this band has been taken to indicate a *trans*-configuration and this test has been applied with success to many [Co en$_2$XY]$^{n+}$ complexes of known configuration. It must be realised, however, that whereas a single peak indicates a *trans*-configuration, a split peak does not necessarily indicate a *cis*-configuration.

Therefore, from their infrared spectra and from their behaviour with resolving agents, it is concluded that all the monocyanobisethylenediaminecobalt(III) complexes described in this paper have a *trans*-configuration. It must be admitted, however, that the evidence, although reasonable, is not yet conclusive.

EXPERIMENTAL

Reaction between trans-*Dichlorobisethylenediaminecobalt*(III) *Chloride and Potassium Cyanide in Concentrated Solution.*—(*a*) The salt, *trans*-[Co en$_2$Cl$_2$]Cl (14·3 g.), in water (30 ml.) at room temperature was treated with potassium cyanide (3·3 g.) in water (10 ml.). Heat was evolved and, on cooling, the mixture formed a paste of orange-yellow crystals. These were filtered off, washed with alcohol and ether, and air-dried (yield 3 g.). This compound was shown, by its visible absorption spectrum, to be trisethylenediaminecobalt(III) trichloride. The infrared spectrum contained no lines that could be assigned to a cyanide group. The filtrate gave an orange-red deliquescent powder (6 g.) on careful addition of alcohol (Found: C, 19·1; H, 6·9; N, 20·6; Cl, 22·4; Co, (i) 18·3, (ii) 20·4. Calc. for $C_5H_{20}Cl_2CoN_5O_2$: C, 19·3; H, 6·5; N, 22·5; Cl, 22·7; Co, 18·9%). The cobalt analyses are estimated from the residues from (i) the carbon and hydrogen analyses and (ii) the nitrogen analysis, assumed to be Co_2O_3.

(*b*) The salt, *trans*-[Co en$_2$Cl$_2$]Cl (14·3 g.), was dissolved in water (60 ml.) at 0° and the solution was treated, dropwise, with an ice-cold solution of potassium cyanide (3·3 g.) in water (10 ml.) (the extra water was necessary because of the reduced solubility of the complex at 0°). Alcohol was added carefully and the orange-red solid was precipitated (8 g.). The trichloride, [Co en$_3$]Cl$_3$, which should be precipitated under these conditions, could not be detected.

Other Preparations.—*trans*-Dichlorobisethylenediaminecobalt(III) chloride was prepared by Bailar and Rollinson's method.[13]

cis-*Dicyanobisethylenediamine cobalt*(III) *thiosulphate* was prepared from the salt Na[Co en$_2$(S$_2$O$_3$)$_2$] by Ray's method.[5] The crude product was recrystallised from hot water. (Found: Co, 19·8. $C_6H_{16}CoN_6O_3S_2,H_2O$ requires Co, 19·9%). The yield was low and the mixture contained a large amount of [Co en$_3$]$^{3+}$ salts.

cis-*Dicyanobisethylenediaminecobalt*(III) *chloride* was prepared by evaporating a mixture of the thiosulphate (3 g.) and concentrated hydrochloric acid (30 ml.) to dryness on a steam-bath. Water (25 ml.) was then added and the solution filtered to remove sulphur. The pure crystalline chloride was isolated by carefully adding alcohol [Found: Co, 22·0; Cl$^-$, 13·3. $C_6H_{16}CoClN_6$ requires Co, 22·0; Cl$^-$, 13·3%).

(+)-cis-*Dicyanobisethylenediaminecobalt*(III) (+)-*α-bromocamphor-π-sulphonate* was prepared

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[13] Bailar and Rollinson, *Inorg. Synth.*, 1946, **2**, 223.

by treating a 10% aqueous solution of the racemic chloride with a cold saturated solution of ammonium (+)-α-bromocamphor-π-sulphonate and cooling the mixture in ice. The crystals obtained were filtered off, washed with alcohol and ether, and dried (Found: Co, 10·8. $C_{16}H_{30}BrCoN_6O_4S$ requires Co, 10·9%).

This salt (5 g.) was ground with concentrated hydrochloric acid (20 ml.) and the resulting solid was filtered off and washed with alcohol and ether. The active *chloride* was recrystallised by dissolving it in the minimum amount of warm water and then adding alcohol (Found: Co, 21·8; Cl^-, 13·2%). It was reconverted into the α-bromocamphorsulphonate which in turn was reconverted into the active chloride. This cycle of operations did not change $[M]_D$ (+66°) of the chloride and so it was concluded that the resolution was complete in the first operation.

Cyanosulphitobisethylenediaminecobalt(III). A 10% aqueous solution of chlorosulphitobisethylenediaminecobalt(III) [14] was treated with an equivalent amount of potassium cyanide dissolved in the minimum amount of water. The mixture was filtered and alcohol was added. The crystalline *complex* obtained was filtered off, washed with alcohol and ether, dried, and recrystallised by dissolution in the minimum amount of water at room temperature and addition of alcohol (Found: Co, 19·4; loss in wt. on drying, 5·7. $C_5H_{16}CoN_5O_3S,H_2O$ requires Co, 19·4; H_2O, 5·9%).

trans-*Chlorocyanobisethylenediaminecobalt*(III) *chloride*. The complex $[Co\ en_2(SO_3)CN]$ was dissolved in the minimum amount of concentrated hydrochloric acid. Sulphur dioxide was evolved and crystalline *salt* was slowly deposited. This was filtered off, washed with alcohol and ether, dried, and recrystallised by dissolution in the minimum volume of 6N-hydrochloric acid and addition of alcohol (Found: Co, 19·9; co-ordinated Cl, 12·1; Cl^-, 12·1; loss of wt. on drying, 6·1. $C_5H_{16}Cl_2CoN_5,H_2O$ requires Co, 20·0; co-ordinated Cl, 12·1; Cl^-, 12·1; H_2O, 6·1%).

The same compound was obtained when the sulphito-complex was decomposed by alcoholic hydrochloric acid; the chlorocyano-complex was recovered unchanged when its aqueous solution was allowed to evaporate slowly to dryness at room temperature.

trans-*Chlorocyanobisethylenediaminecobalt*(III) *nitrate* was prepared by mixing concentrated aqueous solutions of the complex chloride and ammonium nitrate. The crystals were filtered off, washed with alcohol and ether, and dried (Found: Co, 19·3; co-ordinated Cl, 11·6; Cl^- absent. $C_5H_{16}ClCoN_6O_3$ requires Co, 19·4; co-ordinated Cl, 11·7%).

The *cyanide* was prepared in an analogous way by using potassium cyanide (Found: Co, 20·6; co-ordinated Cl, 12·5; CN^-, 9·2. $C_6H_{16}ClCoN_6,H_2O$ requires Co, 20·6; co-ordinated Cl, 12·5; CN^-, 9·1%).

The *thiocyanate* was prepared analogously (Found: Co, 19·5; Cl, 11·8; SCN^-, 19·4. $C_6H_{16}ClCoN_6S$ requires Co, 19·7; Cl, 11·9; SCN^-, 19·4%).

The *nitrite* was likewise made by using sodium nitrite (Found: Co, 20·5; Cl, 12·5. $C_5H_{16}ClCoN_6O_2$ requires Co, 20·5; Cl, 12·4%).

The *sulphate* was prepared by adding solid ammonium sulphate to a concentrated solution of the chloride (Found: Co, 19·2; Cl, 11·8. $C_5H_{16}ClCoN_5O_4S,2H_2O$ requires Co, 19·2; Cl, 11·6%).

The *perchlorate* was similarly prepared by using solid sodium perchlorate (Found: co-ordinated Cl, 10·4. $C_5H_{16}Cl_2CoN_5O_4$ requires co-ordinated Cl, 10·4%).

The *dithionate* was prepared by using solid sodium dithionate (Found: Co, 18·3. $C_{10}H_{32}Cl_2Co_2N_{10}O_6S_2$ requires Co, 18·3%).

The *bromide* was prepared by using solid sodium bromide (Found: Co, 18·3; Cl, 11·1; Br^-, 24·8. $C_5H_{16}BrClCoN_5$ requires Co, 18·3; Cl, 11·1; Br^-, 24·9%).

trans-*Chlorocyanobisethylenediaminecobalt*(III) (+)-*α-bromocamphor-π-sulphonate* was prepared by mixing an aqueous solution of the chloride with small portions of an aqueous solution of 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, 10·7. $C_{15}H_{30}BrClCoN_5O_4S$ requires Co, 10·7%). The bromocamphorsulphonate was converted into the chloride by grinding it with concentrated hydrochloric acid but the recrystallised product was not optically active.

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[14] Baldwin, *J.*, 1961, 3123.

trans-*Aquocyanobisethylenediaminecobalt*(III) *nitrate*. The chloride, *trans*-[Co en_2(CN)Cl]Cl,H_2O (5 g.), was dissolved in water (25 ml.) and to it was added aqueous silver nitrate (5·8 g. in 25 ml.). The mixture was kept at 25° for 15 hr. and then filtered. Alcohol and ether were added and the crystals obtained were filtered off, washed with alcohol and ether, and air-dried. The *complex* was purified by adding ethanol to its aqueous solution and repeating the process until the visible absorption spectrum of the product was reproducible (usually two recrystallisations sufficed) (Found: Co, 16·9. $C_5H_{18}CoN_7O_7$ requires Co, 17·0%).

The derived *perchlorate* was obtained by adding solid sodium perchlorate to an aqueous solution of the nitrate (Found: equiv., 211. $C_5H_{18}Cl_2CoN_5O_9$ requires equiv., 211). The identity of the visible absorption spectra of the nitrate and the perchlorate was taken as evidence of isomeric purity.

trans-*Hydroxocyanobisethylenediaminecobalt*(III) *chloride*. The chloride, *trans*-[Co en_2(CN)Cl]Cl,H_2O (11 g.), was treated with a solution of lithium hydroxide monohydrate (1·8 g.) in water (11 ml.) and, when the solid had all dissolved, the solution was filtered. Methanol (33 ml.) was added and the crystals formed were filtered off, washed with alcohol and ether, and air-dried. The *product* was not improved by further recrystallisation (Found: Co, 20·1; OH, 5·8; Cl^-, 12·2. $C_5H_{17}ClCoN_5O,2H_2O$ requires Co, 20·1; OH, 5·8; Cl^-, 12·1%). The hydroxyl group was determined by titrating the complex with standard acid with a glass electrode as indicator. It was concluded from the pH–titre relationship that pK_a of the aquo-complex is 7·45 at 16°. The spectrum of an acidified solution of the hydroxocyano-complex is identical with those of the two-aquocyano-salts.

Measurements.—Visible absorption spectra were measured with a Unicam S.P. 500 quartz spectrophotometer. Infrared measurements were made with a Perkin-Elmer Infracord model 137 spectrometer. Polarimetric measurements were made visually with a Hilger and Watts mark III polarimeter and a sodium lamp. The fast sampling technique and the apparatus used in the study of the cyanide reactions have been described elsewhere.[8]

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