315. cis-trans-*Interconversion amongst Co-ordination Compounds. Part I. Investigation of the Isomeric Dichlorobisethylenediaminocobaltic Chlorides by Means of a Radioactive Isotope of Chlorine.*

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It has long been known that green 1 : 6-[Co en_2Cl_2]Cl changes into violet 1 : 2-[Co en_2Cl_2]Cl on evaporation of the aqueous solution to dryness, and that the reverse transformation is promoted by hydrochloric acid. The mechanism of interconversion has remained a matter of conjecture. Investigation of the redistribution of the component chlorine ions during isomerisation with the aid of radio-chloride has assisted in clarifying the problem. Intramolecular rearrangement can be disregarded. The immediate result of dissolving the compounds in hot water is the replacement of Cl′ by H_2O within the co-ordination spheres; the original complex ions are re-formed on concentration of the solution by evaporation. The relative amounts of the isomeric chlorides in the solid residue appear to be largely controlled by solubility considerations. The *cis*-chloride is less soluble than the *trans-*; but the latter alone forms a sparingly soluble addition compound with hydrogen chloride. Apart from its function as precipitant, hydrochloric acid plays no essential rôle in the *cis* ⟶ *trans*-change.

Many instances of, supposedly, *cis-trans*-isomerism are to be found amongst the co-ordination compounds of tervalent chromium and cobalt. The transition from one isomeric form to the other is often effected by simple means, but very little consideration has hitherto been given to the mechanism of interconversion; and in some cases the qualitative statements made with regard to isomerisation stand in apparent contradiction to observations on other characteristic reactions of the complex ions. For this reason, and because of the opportunities afforded by the employment of isotopes as " indicators," a general investigation of the problem seems desirable. The present paper deals exclusively with perhaps the best-known example, the transformation of green *trans*-, or 1 : 6-dichlorobisethylenediaminocobaltic chloride, [Co en_2Cl_2]Cl, into the isomeric violet *cis*-, or 1 : 2-salt and *vice versa*. Jörgensen (*J. pr. Chem.*, 1889, **39**, 1; 1890, **41**, 440) discovered that this conversion is brought about by evaporation of the aqueous solution to dryness, and that the reverse process occurs in the presence of hydrochloric acid.

When 1 : 2- or 1 : 6-[Co en_2Cl_2]$^{\cdot}$ is dissolved in water, substitution of H_2O for Cl′ occurs with formation of [Co $en_2(H_2O)Cl$]$^{\cdot\cdot}$ and Co [en_2 $(H_2O)_2$]$^{\cdot\cdot\cdot}$ (Werner and Herty, *Z. physikal. Chem.*, 1901, **38**, 340). Evidence of " aquotisation " is also furnished by Uspensky and Tschibisoff (*Z. anorg. Chem.*, 1927, **164**, 326), who observed that dilute aqueous solutions containing initially the same molar concentrations of 1 : 2- or 1 : 6-[Co en_2Cl_2]Cl, 1 : 2-[Co $en_2(H_2O)Cl$]Cl_2, or 1 : 2- or 1 : 6-[Co $en_2(H_2O)_2$]Cl_3 ultimately give rise to identical absorption spectra, the equilibrium state being rapidly established by boiling. Although the spectrometric method could certainly be applied to greater advantage than was done by these authors, attempts to determine the composition of the solutions by such methods are unsatisfactory, for the situation is further complicated by equilibria such as

$$[\mathrm{Co\ en_2(H_2O)Cl}]^{\cdot\cdot} \rightleftharpoons [\mathrm{Co\ en_2(OH)Cl}]^{\cdot} + \mathrm{H}^{\cdot}$$

(cf. Brönsted, *Z. physikal. Chem.*, 1926, **122**, 383; 1928, **134**, 97). Mathieu's kinetic studies (*Bull. Soc. chim.*, 1936, **3**, 2121, 2152) show that the complex ions 1 : 2- and 1 : 6-$[\text{Co en}_2\text{Cl}_2]^{\cdot}$ are transformed quantitatively in aqueous solution into 1 : 2-$[\text{Co en}_2(\text{H}_2\text{O})\text{Cl}]^{\cdot\cdot}$, the former reaction being half-completed within 30 minutes at 40°, and the latter less rapidly. The next stage of aquotisation, the production of $[\text{Co en}_2(\text{H}_2\text{O})_2]^{\cdot\cdot\cdot}$, proceeds at a slower rate, is retarded by hydrogen ion, and is to some extent reversible, the back reaction being favoured by rise of temperature. Now, since the isomerisation reactions, [1 : 2] $\longleftrightarrow$ [1 : 6],† are carried out in aqueous solution at about 100°, the formation of the "aquo" complex ions must be accepted as inevitable first steps.

Our experiments fall roughly into two categories: (1) the employment of a radioactive chlorine isotope to mark the distribution between the co-ordinatively bound and the free ionic state of chlorine, (2) an investigation of the amounts of [1 : 2] and of [1 : 6] produced under various conditions of isomerisation, a matter which has received surprisingly little attention.

Experiments were carried out at temperatures between 0° and 80° to discover whether exchange occurred between radiochloride ion, *Cl′, and the following complex ions: 1 : 2- and 1 : 6-$[\text{Co en}_2\text{Cl}_2]^{\cdot}$ and 1 : 2-$[\text{Co en}_2(\text{H}_2\text{O})\text{Cl}]^{\cdot\cdot}$. The method consisted in dissolving the complex salt in a solution containing *Cl′, and, after a time, reprecipitating the complex ion and testing for radioactivity. *Direct replacement of co-ordinatively bound chlorine by chloride ion was not observed with any of the complex ions.* The results summarised in Table I show that only with $[\text{H}_2\text{O,Cl}]^{\cdot\cdot}$ at 80° was measurable activity found in the precipitate, at which temperature aquotisation and the reverse process take place rapidly. Clearly, in the absence of direct exchange, the chance of a positive result is greater in this case than for the other two complex ions. Even so, only about 50% of the precipitate contained radio-chlorine. These facts are of interest in several connexions apart from their bearing upon the problem under discussion. For example, it has been found (Jenkins and Johnson, unpublished) that the initial rate of change of rotatory power of *d*-1 : 2-$[\text{Co en}_2\text{Cl}_2]^{\cdot}$ in aqueous solution is somewhat accelerated by potassium chloride. Since it is now certain that the reaction *Cl′ + $[\text{Co en}_2\text{Cl}_2]^{\cdot} \longrightarrow [\text{Co en}_2\text{Cl*Cl}]^{\cdot}$ + Cl′ does not take place, the catalytic influence of potassium chloride cannot be attributed to a process of "inversion by substitution" (cf. Bailar, Haslam, and Jones, *J. Amer. Chem. Soc.*, 1936, **58**, 2226; Bergmann, *ibid.*, 1937, **59**, 423) analogous to that proposed by Olsen (*J. Chem. Physics*, 1933, **1**, 418) and by Meer and Polanyi (*Z. physikal. Chem.*, 1932, **19**, *B*, 164) in the case of carbon compounds.

The change [1 : 6] $\longrightarrow$ [1 : 2] is accomplished by evaporation of a boiling aqueous solution of [1 : 6], but in order to study the rearrangement of the chlorine nuclei, radiochloride ion must be introduced, *e.g.*, Na*Cl. The residue remaining after evaporation contains [1 : 2], [1 : 6], and sodium chloride, and on repeated extraction with small quantities of ice-cold water the last two substances are removed, leaving the relatively insoluble [1 : 2] in nearly pure condition. In some preliminary experiments, the entire chlorine contents of the solid and the liquid extract were separately converted into silver chloride and the radioactivities of equal weights of silver chloride from each compared. In later experiments, the nitrates, $[1:2]\text{NO}_3$ and $[1:6]\text{NO}_3$, were prepared from the residue, and their activities measured. A further comparison was made of the activities of bound chlorine in $[1:2]\text{NO}_3$ from the residue and of the free chloride ion in the aqueous extract. The results (Table II) indicate that complete intermingling of all the chlorine nuclei takes place during isomerisation. The reverse transformation, [1 : 2] $\longrightarrow$ [1 : 6], is brought about by evaporation with hydrochloric acid, which also affords a convenient means of introducing radio-chloride. The dry residue is extracted with cold water, and the aqueous extract poured into nitric acid; the chlorine in the precipitated $[1:6]\text{NO}_3$ is converted into silver chloride and its radioactivity compared with that obtained from a sample of the original acid. An improved method is to pass the hydrogen chloride expelled during evaporation into a solution of silver nitrate, and to compare the activity of the precipitate with

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† 1 : 2- and 1 : 6-$[\text{Co en}_2\text{Cl}_2]\text{Cl}$ will be denoted by the symbols [1 : 2] and [1 : 6] respectively, or, where it is necessary to specify the anion, by [1 : 2]Cl, $[1:6]\text{NO}_3$, etc. The compounds $[\text{Co en}_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ and $[\text{Co en}_2(\text{H}_2\text{O})_2]\text{Cl}_3$ are conveniently represented by $[\text{H}_2\text{O,Cl}]$ and $[(\text{H}_2\text{O})_2]$.

that of the silver chloride derived from [1 : 6]NO_3 obtained from the dry residue. As in the previous case, *the results lead unequivocally to the conclusion that the chloride ions undergo complete random redistribution during the isomeric change.*

As regards the efficiency of the transformation processes, Uspensky and Tschibisoff (*loc. cit.*) state that 40—70% conversion into [1 : 2] occurs on evaporation of [1 : 6] with water. Clearly, the experimental conditions must greatly influence the results. Experiments carried out rapidly, in accordance with the routine adopted when studying isotope exchange (but in the absence of sodium chloride), gave percentages varying from 40 to 55. There appears to be no previous record of quantitative data regarding the process [1 : 2] ⟶ [1 : 6], and our observations on this change are significant. When [1 : 2] is evaporated with different concentrations of hydrochloric acid (0·1—10N), other circumstances being controlled as rigidly as possible, little variation is found in the proportions of the isomeric chlorides in the dry residue (Table III); the actual proportions range from about 70 to 95%, according to the manner in which the last c.c. or so of acid is evaporated. In *pure water* the efficiency of the conversion process may be as high as 75%, but the results of individual experiments fluctuate widely for reasons explained on p. **1496.** The inference is that, contrary to what seems to have been supposed hitherto, hydrochloric acid is not concerned in any fundamental way with the *cis*- to *trans*-change.

Discussion.—The known facts appear to be in agreement with the following dynamic scheme, which refers to an aqueous solution. 1 : 2- and 1 : 6-$[\mathrm{Co\,en_2Cl_2}]^{\cdot} \underset{d}{\overset{a}{\rightleftharpoons}} \mathrm{Cl}' + [\mathrm{Co\,en_2(H_2O)Cl}]^{\cdot\cdot} \underset{c}{\overset{b}{\rightleftharpoons}} 2\mathrm{Cl}' + [\mathrm{Co\,en_2(H_2O)_2}]^{\cdot\cdot\cdot}$. The existence in hot solution of these equilibria accounts for the complete re-shuffling of chloride ions which accompanies isomerisation; the relative rates and participation of reactions *a*, *b*, *c*, and *d*, depend on the circumstances obtaining. The possibility of intramolecular rearrangement, [1 : 2] $\rightleftharpoons$ [1 : 6], is not indicated in the scheme because experiments with mixtures of the isomeric complex ions, one or other of them containing radio-chloride in the co-ordination sphere, have shown that intramolecular change does not occur in either direction at room temperature. Whether it takes place in aqueous solution at 100° cannot be ascertained, since aquotisation will in any case mask the process. Reactions *a* and *b* constitute the initial stages of all experiments outlined in the previous section, the hot solutions rapidly acquiring a purple-red colour irrespective of the *cis*- or the *trans*-configuration of the original material. Isomerisation may be said, in effect, to start from this point. Reactions *c* and *d* (the latter in particular) become important during the final stages of evaporation, in the presence of large concentrations of dissolved substances. The slowness of these reactions is responsible for the failure to achieve more than partial isomerisation by evaporation of solutions at, say, 20°, when the residues invariably contain a large proportion of " aquo " complex ions.

The velocities of the aquotisation reactions *a* and *b* necessarily obey a unimolecular law, either because the rate-determining step is unimolecular, or because the solvent is involved, at constant activity, in a slow bimolecular process. On the other hand, the reverse reactions *c* and *d* can conceivably follow uni- or bi-molecular laws as exemplified by the following equations (reaction *c*):

$$\begin{tikzcd}
{[\mathrm{Co\,en_2(H_2O)_2}]^{\cdot\cdot\cdot} + \mathrm{Cl}'} \arrow[r, "\text{slow}"] \arrow[d, shift left] & {[\mathrm{Co\,en_2(H_2O)Cl}]^{\cdot\cdot}\quad\text{(bimolecular)}} \\
{[\mathrm{Co\,en_2(H_2O)OH}]^{\cdot\cdot} + \mathrm{Cl}'} \arrow[r, "\text{fast}"] \arrow[u, shift left, "\text{slow}"] & {[\mathrm{Co\,en_2(H_2O)Cl}]^{\cdot\cdot}\quad\text{(unimolecular)}}
\end{tikzcd}$$

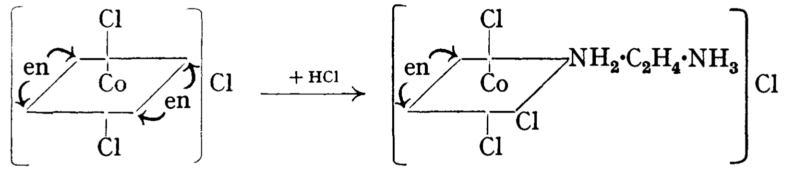
The simultaneous occurrence of both mechanisms perhaps explains Mathieu's inability to decide between a uni- and a bi-molecular law on a basis of measured rate constants. Further discussion of the reactions *c* and *d* in relation to isomerisation is hampered by the incompleteness of the thermochemical and kinetic data, matters which are engaging our attention.

The heat of formation in solution of [1 : 6] is slightly larger than that of [1 : 2] (Ovenston and Terrey, J., 1936, 1660), a fact which Mathieu correlates with their different rates of aquotisation (*loc. cit.*, p. 2152); but [1 : 2] is much less soluble than [1 : 6] and will be precipitated first. There seems no reason to doubt Uspensky and Tschibisoff's tentative conclusion (*loc. cit.*) that the amounts of the two isomeric chlorides in the residues remaining after evaporation are largely controlled by considerations of solubility. Another factor favourable to the production of [1 : 2] is the preponderance in solution of the ion 1 : 2-$[Co\ en_2(H_2O)Cl]^{\cdot\cdot}$ consequent upon the instability of 1 : 6-$[Co\ en_2(H_2O)Cl]^{\cdot\cdot}$, salts of which have not been isolated. Nevertheless, both green and violet salts separate during the final stages of evaporation of aqueous solutions, the proportion of green being larger the quicker the operation. Addition of a soluble chloride, other than hydrogen chloride, improves the yield of [1 : 2] (Table IV). The precipitation of [1 : 6] in spite of contrary influences, together with [1 : 2], points to the existence of at least one slow step in the sequence of events. The situation is conceivably represented as

$$\begin{array}{rcl} 1:2\text{-}[Co\ en_2Cl_2]^{\cdot} + H_2O & \rightleftharpoons & 1:2\text{-}[Co\ en_2(H_2O)Cl]^{\cdot\cdot} + Cl' \\ & & \qquad\Updownarrow \\ 1:6\text{-}[Co\ en_2Cl_2]^{\cdot} + H_2O & \rightleftharpoons & 1:6\text{-}[Co\ en_2(H_2O)Cl]^{\cdot\cdot} + Cl' \end{array}$$

Since isomerisation is a process of synthesis from the "aquo" complex ions, several opportunities occur for the production of alternative configurations. The choice of $[H_2O,Cl]^{\cdot\cdot}$ appears to have some justification. As noted on p. 1491, the water molecule entering [1 : 2] occupies the position vacated by chloride ion and the probability is that aquotisation of [1 : 6] takes place in similar fashion. Indeed, Mathieu (*Bull. Soc. chim.*, 1937, **4**, 687) has proved that simple substitution of water molecules for co-ordinated anions is the general rule. The assumption of a finite, though small, concentration of 1 : 6-$[H_2O,Cl]^{\cdot\cdot}$ is in harmony with the facts of isomerisation and not inconsistent with the failure to isolate its salts. Furthermore, Mathieu (*ibid.*) has observed that *d*-1 : 2-$[H_2O,Cl]^{\cdot\cdot}$ undergoes slow racemisation in solution at room temperature, quite independently of the process of aquotisation. A reasonable explanation is the intermediate formation of 1 : 6-$[H_2O,Cl]^{\cdot\cdot}$. Intramolecular rearrangement within the co-ordination sphere of a complex ion is a rare phenomenon, but one example for which the experimental evidence appears conclusive is the racemisation of chromioxalate, $[Cr(C_2O_4)_3]'''$ (Johnson *et al.*, *Trans. Faraday Soc.*, 1935, **31**, 1612; Long, *J. Amer. Chem. Soc:*, 1939, **61**, 570). Finally, the equilibrium postulated between the *cis*- and the *trans*-form of the chloro-aquo ion will entail a greater concentration of the latter form at 100° than at room temperature, a consideration of obvious importance to the matters under discussion.

An experimental result which strenthens the views already put forward is the following: if, instead of [1 : 6]Cl, the nitrate $[1:6]NO_3$ is dissolved in hot water (aquotisation occurs) and the solution is evaporated to dryness, the residue is green, without a trace of violet $[1:2]NO_3$. Thus, *isomerisation of* trans-*dichlorobisethylenediaminocobaltic nitrate does not occur.* Conversely, $[1:2]NO_3$ is by the same procedure converted quantitatively into $[1:6]NO_3$. Now the latter is very sparingly soluble in water, much less soluble than $[1:2]NO_3$ or [1 : 2]Cl, and nitrate ion has little tendency to enter the co-ordination sphere. Therefore, NO_3' does not compete successfully with Cl′ in displacing H_2O from the "aquo" complex ions during evaporation, and as soon as even a small concentration of $[1:6]^{\cdot}$ is formed the nitrate is precipitated. Again, solubility is the controlling factor in the preparation of [1 : 6], the presence of hydrochloric acid in solution causing precipitation of the hydrochloride (Jörgensen, *loc. cit.*), usually formulated as 1 : 6-$[Co\ en_2Cl_2]Cl,HCl$. On the other hand, Drew and Pratt (J., 1937, 506) attribute a deeper significance to the formation of the hydrochloride and state, though without positive evidence, that addition of hydrogen chloride to [1 : 6] involves the rupture of a chelate link between ethylenediamine and the cobalt nucleus:



These authors explain isomerisation by postulating analogous intermediate compounds through addition of water to [1 : 6] and of hydrogen chloride to [1 : 2] (although the latter does not form a hydrochloride) and, in like manner, other cases in which substitution in the co-ordination sphere produces a change of configuration. The merits of this hypothesis must be judged by consideration of individual cases. Objections can be brought against its application to the compounds under discussion. First, hydrogen chloride is very easily removed from the hydrochloride, either by heating the solid, or dissolving it in water, or washing it with alcohol. Large green crystals left undisturbed in a dry atmosphere lose hydrogen chloride superficially, the process commencing at points on the surface and spreading in circular patches somewhat resembling the dehydration nuclei of chrome alum crystals (Cooper and Garner, *Trans. Faraday Soc.*, 1936, **32**, 1739). Furthermore, the loss of hydrogen chloride from the crystals is accompanied by total reversion to [1 : 6], an observation contrary to the implications of Drew and Pratt's formula; for in all other instances their hypothesis is designed to explain a change of configuration. Be it noted that the colours of the *trans*-salt and of the hydrochloride are merely different shades of green. The problem was attacked with radio-chlorine in the following way. Radioactive [1 : 6], *i.e.*, $[Co\ en_2{}^*Cl_2]^*Cl$, the asterisks denoting a uniform distribution of the radio-isotope within and without the co-ordination sphere, was prepared and reprecipitated from cold solution as $[Co\ en_2{}^*Cl_2]Cl,HCl$ by addition of a large excess of hydrochloric acid. The hydrogen chloride was expelled from the crystals by heat and passed into silver nitrate. The silver chloride proved to be devoid of activity, a result which, whilst fully anticipated, is not without value.

Although Jörgensen's formula is probably inadequate, there appear to be no grounds for differentiating sharply between the condition of HCl in the hydrochloride and that of H_2O in, say, [1 : 2] monohydrate, usually represented as 1 : 2-$[Co\ en_2Cl_2]Cl,H_2O$. Clearly, the proved racemic character of the latter compound is not expressed by the formula $[Co\ en(enH)Cl_2OH]Cl$. Drew and Pratt assume the intermediate formation of such an addition compound in the *trans* ⟶ *cis* change. Our results suggest that water molecules normally participate in the process *cis* ⟶ *trans*; there is no evidence whatever of association between [1 : 2] and HCl. Mathieu (*loc. cit.*, 1937) has shown, from studies of optical rotatory dispersion, that aquotisation of [1 : 2] occurs through direct replacement of chloride by water *without change of configuration, i.e.*, *d*-1 : 2-$[Co\ en_2Cl_2]^{\cdot} \longrightarrow$ *d*-1 : 2-$[Co\ en_2(H_2O)Cl]^{\cdot\cdot}$. Drew and Pratt's mode of substitution would give rise to a racemic mixture (together with *trans*?) and hence it cannot be invoked to explain the conversion of *cis* into *trans*. Their views in regard to both the structure of the *trans*-hydrochloride and the mechanism of isomerisation therefore receive very little support from established facts.

EXPERIMENTAL.

Preparations.—*trans*-Dichlorobisethylenediaminocobaltic chloride, obtained by Bräunlich's modification (*Z. anorg. Chem.*, 1900, **22**, 123) of Jörgensen's method (*loc. cit.*), was purified from yellow $[Co\ en_3]Cl_3$ by recrystallisation from hot concentrated hydrochloric acid (Found : Cl, 37·3. Calc. : Cl, 37·3%). This was converted into the *cis*-isomer by evaporation of an aqueous solution at 100°, the residue being extracted with aqueous alcohol until a cold saturated solution of the violet solid when poured into nitric acid (3 vols. of conc. acid : 4 vols. of water; referred to as " standard ") and kept for 20 mins. gave no trace of green precipitate (Found : H_2O, 6·1; Cl, 34·8. Calc. for $[Co\ en_2Cl_2]Cl,H_2O$: H_2O, 5·95; Cl, 35·1%). $[Co\ en_2(H_2O)Cl]SO_4,2H_2O$ was prepared by Werner's method (*Annalen*, 1912, **386**, 122); it contained a trace of chloride (Found : H_2O, 9·47; Cl, 10·1; SO_4, 25·1. Calc. : $2H_2O$, 9·88; Cl, 9·73; SO_4, 26·3%).

Radio-chlorine.—The radioactive isotope was prepared by use of an intimate mixture of powdered metallic beryllium and radium chloride : ${}^{35}_{17}Cl + {}^{1}_{0}n \longrightarrow {}^{36}_{17}Cl$. Our recording apparatus, Geiger–Müller counter, etc., has been described by Hamblin and Johnson (*Phil. Mag.*, 1937, **24**, 553). The yield of radio-chlorine was poor compared, say, with that of radio-bromine or radio-iodine in similar circumstances. This was to some extent offset by (1) use of Szilard and Chalmer's method (*Nature*, 1934, **134**, 462) to concentrate the active isotope; carbon tetrachloride was the liquid employed, irradiation with neutrons lasting 3—4 hours; (2) working with small amounts of materials (thus obtaining relatively high intrinsic radioactivities); and (3) spreading the compound under examination, usually silver chloride, mixed with an adhesive, upon the inside of a cylinder of cartridge-paper which was slipped over the Geiger counter. The substance was sprinkled uniformly over a prescribed gummed area before the cylinder was rolled. With careful attention to details, this method gave reproducible and quantitatively satisfactory results; *e.g.*, the " count " was shown to be proportional to the concentration of radio-chloride in the silver chloride. The identity of the active isotope was established by irradiating a solution of sodium chloride with neutrons, taking the chloride through a sequence of different reactions, ultimately recovering it as silver chloride, and showing that the activity was virtually identical with that of a sample prepared from the original substance. The unstable phosphorus isotope $^{32}_{15}P$ (decay period $\bumpeq$ 14 days) was produced along with $^{36}_{17}Cl$ but was not precipitated by silver nitrate from acid solutions. The possible formation of radio-sulphur was investigated but not confirmed.

Isotope Exchange with Complex Salts.—Means had to be found for effecting rapid precipitation of the three complex ions from dilute solutions, since, on account of aquotisation, their concentrations fell progressively during experiments. The ion $[1:6]^{\cdot}$ is best precipitated as the nitrate with " standard " nitric acid (see above); the more soluble $[1:2]NO_3$ can be recovered from solutions containing it and the " aquo " complex ions by pouring into a large volume of aqueous alcohol (65% ethyl alcohol) saturated with ammonium nitrate. The sulphate, $[H_2O,Cl]SO_4,2H_2O$, separates fairly quickly on addition, with vigorous stirring, to aqueous alcohol (as above) saturated with ammonium sulphate, or to a mixture of equal parts of absolute alcohol and ether. The chlorine in each of these compounds is inside the co-ordination sphere; hence the precipitates can be presented to the Geiger counter directly, with consequent saving of time and " activity." Control experiments proved that the observed activities of the complex salts and of silver chloride derived from them, containing equal weights of chlorine, were practically identical. The results of exchange experiments are summarised in Table I, *t* denoting the time between mixing the complex salt with radio-chloride (Na^*Cl, $NH_4{}^*Cl$, or H^*Cl) and reprecipitation.

TABLE I.

Temp.	*t*.	Activity of ppt.	Temp.	*t*.	Activity of ppt.	Temp.	*t*.	Activity of ppt.
$1:2\text{-}[Co\,en_2Cl_2]^{\cdot}$			$1:6\text{-}[Co\,en_2Cl_2]^{\cdot}$			$1:2\text{-}[Co\,en_2(H_2O)Cl]^{\cdot\cdot}$		
30°	25 mins.	nil	0°	80 mins.	nil	18°	20 mins.	nil
60	1·25 mins.	,,	60	1·75 mins.	,,	60	2·25 mins.	,,
80	15 secs.	,,	80	25 secs.	,,	80	35 secs.	small

Because of aquotisation, the maximum time (*t*) allowable is conditioned by the temperature, since enough of the complex ion must be recovered for investigation of its radioactivity. Temperature-independent factors which must also be considered are the activity and the decay period (36 mins.) of the chlorine isotope.

cis ⟶ trans-*Conversion.*—The experimental methods have already been outlined. These involved a large number of operations, and consequently nearly 90 mins. elapsed between the removal of the chloride from the neutron-source and the initial observations on the activities of samples of silver chloride. The results of representative experiments are briefly recorded in Table II. The " maximum activities " represent the number of impulses registered by the counter *per minute* averaged over the first 4 mins. of observation; in any one experiment, they are likely to be less concordant than the figures averaged over the whole counting-time (" mean activities "), which was usually about an hour. All activities were corrected for coincident impulses (Todd, *Phil. Mag.*, 1937, **24**, 572), and the " background " was subtracted.

TABLE II.

Isomerisation.	No. of expt.	Activity of equal weights of AgCl prepared from : NaCl in residue. Activity.		[1 : 2] in residue. Activity.		[1 : 6] in residue. Activity.	
		Maximum.	Mean.	Maximum.	Mean.	Maximum.	Mean.
trans	1	77	44	71	42	—	—
↓	2	62	38	61	38	—	—
cis	3	—	—	45	27	48	26
	4	—	—	65	40	65	41
	5	63	42	64	41	64	41
		HCl volatilised					
cis	6	60	43	—	—	66	40
↓							
trans	7	66	46	—	—	61	45

Details of expt. 4 are given in illustration. A solution containing radioactive sodium chloride (0·081 g. in 10 c.c.) was evaporated to dryness with 0·6 g. of [1 : 6]. The residue, when cool, was extracted thrice with successive amounts (1 c.c.) of cold water, filtered rapidly, and the filtrate allowed to drop into " standard " nitric acid. The green precipitate of [1 : 6]NO_3 was filtered off, washed with nitric acid, transferred to a beaker with water (60 c.c.), and boiled. Silver nitrate (5 c.c. of 20% solution) was added to the boiling solution, and the heating continued for 7 mins. before filtering the solution. The violet residue of [1 : 2] was washed with aqueous alcohol (1 : 3) to remove any remaining sodium chloride and [1 : 6], and treated exactly as above. Both samples of silver chloride were carefully dried, and equal weights (0·2 g.) spread on cartridge-paper cylinders for presentation to the Geiger counter. The prolonged boiling of the silver chloride precipitates brought them to the same physical condition, an essential requirement for accurate comparison of their radioactivities.

Efficiency of cis-trans-*Interconversion.*—In order to discover the best means of determining the proportion of each isomer present in residues after evaporation, control experiments were carried out with mixtures of known composition. The following method was finally adopted. The mixture was extracted with 6 successive amounts (1 c.c.) of cold water, and the extracts filtered into " standard " nitric acid (20 c.c.); after 15 mins.' stirring, the precipitate of [1 : 6]NO_3 was filtered off, washed with absolute alcohol, dried by cautious heating, and weighed. The percentage conversion occurring during isomerisation was investigated, all evaporations being conducted in accordance with a definite routine.

(a) cis ⟶ trans-*Conversion.* The *cis*-compound used gave no indication of the presence of *trans*- by the nitric acid test. Evaporation was carried out with 0·5 g. in 10 c.c. of hydrochloric acid, and occupied 12 mins. Slight differences in the conditions of evaporation during the final stages are chiefly responsible for the lack of reproducibility. The results are given in Table III.

TABLE III.

HCl, N	10	2	0·5	0·1	0 (pure water)
[1 : 6], %, in residue	80—98	70—95	70—95	65—90	40—75

(b) trans ⟶ cis *Conversion.* 0·5 G. of [1 : 6] was evaporated with 10 c.c. of water, or a solution of sodium chloride. In expts. 6, 7, and 8 (Table IV), the final stage of evaporation was taken very slowly with constant stirring.

TABLE IV.

Expt. no.	1	2	3	4	5	6	7	8	9	10
[1 : 2], %, in residue	48	30	40	62	55	85	74	84	91	85
Time of evapn. (mins.)	12	12	12	12	12	30	30	30	12	12
Wt. of NaCl added (g.)	0	0	0	0	0	0	0	0	0·5	0·5

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