546. *Mechanism, Kinetics, and Stereochemistry of Octahedral Substitutions. Part I. Edge-displacement as a Hypothesis linking Mechanism with Stereochemistry of Substitution.*

By D. D. Brown, C. K. Ingold, and R. S. Nyholm.

Owing to the differing geometry of the octahedron and tetrahedron, there is not a one-to-one correlation for substitution in octahedral molecules, as there is for tetrahedral, between the steric course of an individual molecular act of substitution and the steric course of substitution considered as defining the observable stereochemical relation between product and factor. The degree of correlation between the molecular and observable (microchemical and macrochemical) steric course of substitutions in octahedral molecules is defined, as a first step in setting up the problem of elucidating the circumstances which control the steric course in either sense of octahedral substitutions.

Analogy with carbon chemistry suggests that this problem is unlikely to be soluble without prior elucidation of the main mechanisms available for octahedral substitution, and the establishment of criteria for recognising them. A survey of the literature of octahedral substitutions suggests that some sort of duplexity of mechanism, which might well be a coexistence of the bimolecular and unimolecular mechanisms of nucleophilic substitution, is general.

(1) *The Stereochemical Problem.*

(1*a*) *Types of Observed Stereo-change.*—Werner, more than 40 years ago, investigated the stereochemistry of substitutions at a six-co-ordinated atom. He showed that some substitutions involved *cis-trans*-changes while others preserved a *cis-* or *trans*-configuration. Ever since then, the problem has awaited solution, as to what controls the steric course of substitutions at octahedrally co-ordinated centres.

Werner dealt largely with nucleophilic substitutions, which introduced a group Y in place of a ligand X in the complex of a sexacovalent atom M, for instance, cobalt, having four similar non-replaced ligands R, such as four ammonia or two ethylenediamine molecules, as well as a non-replaced ligand A :

$$\mathrm{Y^- + MR_4AX \longrightarrow MR_4AY + X^-} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (S_N)$$

In the series of bisethylenediaminecobalt(III) complexes, he obtained every possible kind of stereochemical result, as the following examples illustrate (*Annalen*, 1912, **386**, 1) :

$$\textit{cis}\text{-}[\mathrm{Co\ en_2(NH_3)Br}]^{++} \xrightarrow{\mathrm{NH_3}} \textit{cis}\text{-}[\mathrm{Co\ en_2(NH_3)_2}]^{+++}$$

$$\textit{cis}\text{-}[\mathrm{Co\ en_2Cl(NH_3)}]^{++} \xrightarrow{\mathrm{SCN^-}} \textit{trans}\text{-}[\mathrm{Co\ en_2Cl(NCS)}]^{+}$$

$$\textit{trans}\text{-}[\mathrm{Co\ en_2Cl(NH_3)}]^{++} \xrightarrow{\mathrm{NO_2^-}} \textit{trans}\text{-}[\mathrm{Co\ en_2Cl(NO_2)}]^{+}$$

$$\textit{trans}\text{-}[\mathrm{Co\ en_2(NH_3)Cl}]^{++} \xrightarrow{\mathrm{OH^-}} \textit{cis}\text{-}[\mathrm{Co\ en_2(NH_3)(OH)}]^{++}$$

Bailar and his co-workers have emphasized another espect of the matter. By treating the *l-cis*-dichlorobisethylenediaminecobalt(III) ion in aqueous solution with excess of silver carbonate, they could obtain the *l*-carbonatobisethylenediaminecobalt(III) ion (Bailar and Auten, *J. Amer. Chem. Soc.*, 1934, **56**, 774; Bailar, Jonelis, and Hoffman, *ibid.*, 1936, **58**, 2224), although, as Werner and McCutcheon had shown previously, the action of potassium carbonate in water produced the *d*-carbonato-ion * (*Ber.*, 1912, **45**,

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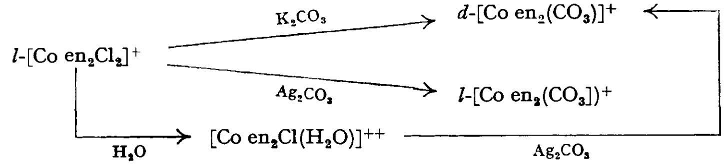
* For purposes of identification, Werner's prefixes, *d* and *l*, are employed, essentially as historical dockets. There are difficulties in labelling by sign of rotation, (+) and (—), since sign often depends on wave-length. Thus the above *l*-dichloro-ion is (—) to cadmium red, but (+) to sodium yellow light. The subject is not advanced enough to justify an attempt to employ configurational symbols, such as *D* and *L*, for the labelling of specific substances.

3281). On keeping the aqueous solution of the *l*-dichloro-ion before adding the silver carbonate, the *d*-carbonato-ion was obtained (Bailar and Peppard, *J. Amer. Chem. Soc.*, 1940, **62**, 820). This altered result is due to the intervention of an additional stage of substitution, namely, monoaquation of the dichloro-ion, as is made clear by comparison of the known rate of this process (Mathieu, *Bull. Soc. chim.*, 1936, **3**, 2121, 2151) with the variations of rotation of the formed carbonato-ion with time of previous keeping of the dichloro-solution :

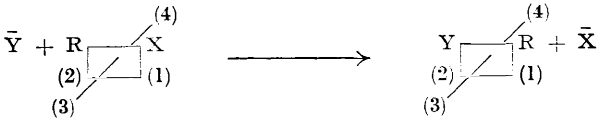


The *l*-dichloro-ion was also converted into the *cis*-diammino-ion with either the *d*- or the *l*-form in excess, by treatment with liquid ammonia at suitably regulated temperatures (Bailar, Haslam, and Jones, *J. Amer. Chem. Soc.*, 1936, **58**, 2226) :

$$l\text{-[Co en}_2\text{Cl}_2]^+ \xrightarrow{\text{NH}_3} \text{either } d\text{- or } l\text{-[Co en}_2(\text{NH}_3)_2]^{+++}$$

These conversion schemes obviously involve changes of configuration, though we cannot with certainty locate the latter.

(1*b*) *Edge-displacement as a Unifying Hypothesis.*—Bailar and his co-workers have claimed the described changes as the first Walden inversions of inorganic chemistry; but the implied correspondence to inversion in organic chemistry is misleading. Not only does it suggest a geometrical inversion of the covalencies, a more radical reorganisation than need be assumed, but also it implies a deeper distinction than can justifiably be drawn between *d*–*l*-conversions and *cis*–*trans*-changes in octahedral substitutions. These *d*–*l*- and *cis*–*trans*-changes are not as different as are some similarly described changes of carbon compounds : either type of change can arise in the octahedral system as a result of what we may call *edge-displacement*, which can be represented thus :



How we observe, and how we describe this change depends, not on the groups Y, R, and X directly concerned, but on the position of some unaffected group A, whose relation to the replaced and replacing groups X and Y is being denoted by the prefixes *d* and *l*, or *cis* and *trans*. If A is at (1), we shall describe the above process as *cis* ⟶ *trans*, if at (2), as *trans* ⟶ *cis*, and if at (3) or (4), as either *d* ⟶ *l* or *l* ⟶ *d*. But the substitution is of just the same stereochemical nature in all cases.

We may, then, look upon changes either of optical or of geometrical configuration as manifestations of a single stereochemical mode of substitution, that of edge-displacement. However, it is to be noticed that, although any observed stereo-change can be understood as an edge-displacement, an observed absence of a stereo-change in octahedral substitution does not always imply the absence of an edge-displacement. If, in the preceding diagram, the groups in positions (1) and (2), and likewise those in positions (3) and (4), can be superposed either on the other by a rotation of the molecule, then in the represented substitution with edge-displacement, a *cis*-factor will give a *cis*-product, chemically identical with that which would be given by substitution without edge-displacement. If the above geometrical condition is satisfied, together with the further condition that the groups in positions (3) and (4) cannot be superposed either on the other by reflexion, then the substitution with edge-displacement will convert a *D*-*cis*-factor into a *D*-*cis*-product, or an *L*-*cis*-factor into an *L-cis*-product, optically, as well as chemically, identical with the product which would be formed in substitution without edge-displacement.* Such is the case, for instance, when the positions (1) and (3) and the positions (2) and (4) are identically coupled, as by ethylenediamine molecules. Thus the experimental fact, that substitution sometimes occurs without stereo-change, does not lead, without further consideration, to the conclusion that substitution can occur without edge-displacement.

However, a *trans*-compound, MR_4AX, on substitution with edge-displacement must yield a *cis*-product MR_4AY; for one of the R's will take the place of X, while Y will take the place of the R, and all four R's were originally *cis*- with respect to A. Therefore an observation that a *trans*-factor yields a *trans*-product does imply substitution without edge-displacement. Now Werner observed several *trans* ⟶ *trans* substitutions; and therefore we may provisionally conclude † that octahedral substitution can occur both with and without edge-displacement. Thus we should expect stereochemical laws for octahedral substitutions at least as complicated as those of tetrahedral substitutions, which in carbon chemistry may occur both with and without inversion.

From the above discussion it will be clear that the fields of incidence of stereo-change and of edge-displacement are not co-extensive. The relation between them for the structures of concern to us here is schematically shown in Table 1. The importance of appreciating the difference between the ranges of incursion of observable stereo-change and of edge-displacement is that the latter, referring, as it does, to a process, rather than immediately to the product, is likely to be the more intimately related to substitution mechanism, and therefore to be subject to simpler stereochemical laws dependent on mechanism, than any which could be framed for direct application to observed stereo-change.

TABLE 1. *Relation of stereo-change to edge-displacement in nucleophilic substitutions in octahedral complexes* MR_4AX.

<table>
<tr><td colspan="2"></td><td colspan="3">Substitution without edge-displacement</td></tr>
<tr><td colspan="2">Stereo-change</td><td colspan="3">No stereo-change</td></tr>
<tr><td><i>cis</i> ↔ <i>trans</i></td><td><i>D</i> ↔ <i>L</i></td><td><i>D</i> ↔ <i>D</i>
<i>L</i> ↔ <i>L</i></td><td><i>cis</i> ↔ <i>cis</i></td><td><i>trans</i> ↔ <i>trans</i></td></tr>
<tr><td colspan="4">Substitution with edge-displacement</td><td></td></tr>
</table>

Werner having established changes of configuration during octahedral substitutions, it seems curious that so many configurations should have been assigned on the assumption that no stereo-changes are involved in the conversions which form the basis of the assignment. Werner himself slipped slightly from rigour in that, in several cases in which a genetic chain admits more than one stereochemical interpretation, he adopts the one with the smallest number of stereo-changes, as though there were some natural law of economy in such changes. However, the blind eye has been turned on possible stereo-changes so much since, that an appreciable proportion of present assignments of configuration cannot be trusted. We known that Erdmann's salt, $NH_4^+[Co(NH_3)_2(NO_2)_4]^-$, was regarded as a *cis*-diammine, because by substitution it gave an optically resolvable and therefore *cis*-diammino-oxalato-salt, $NH_4^+[Co(NH_3)_2(NO_2)_2(C_2O_4)]^-$, until Wells showed by *X*-ray analysis that the original substance is a *trans*-diammine (*Z. Krist.*, 1936, **95**, 74). We have taken the view that, for our purposes, configurations are certain which are based on any of the following criteria : (1) *X*-ray analyses, provided that we have spectral or other evidence that no change of stereo-form occurs between the crystal state and solution, (2) a distinction

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* Capital-letter prefixes are here employed, since the reference is to configurational relationships.

† " Provisionally " because, in the absence of kinetic data, we have no proof that the *trans* ⟶ *trans* substitutions described by Werner go in one step, that is, without an intermediate solvolytic substitution, *i.e.*, aquation.

of optical resolvability, and (3) a genetic chain which does not involve the breaking of a ligand–metal bond.

(2) *The Problem of Substitution Mechanism.*

The stereochemical problem has now been set up in a form convenient for further treatment. But, as the history of the corresponding task of carbon chemistry suggests, the treatment is unlikely to make rapid headway, unless the problem of substitution mechanism is simultaneously solved. For if more than one mechanism operates, each will have its own spatial rules; and then, the unsifted stereochemical observations will give no answer: they must be separated according to mechanism. Therefore our next proceeding is to consider existing evidence for multiplicity of mechanism in octahedral substitutions.

(2*a*) *Indications of a Bimolecular Mechanism of Octahedral Substitution.*—The kinetics of octahedral substitutions have been studied by a number of authors, but the whole of the work has been done in solvent water, whose molecules have a higher nucleophilic (complexing) power towards the ions of transition metals than have the molecules of any other common solvent, except liquid ammonia. It may be on this account that the only substituting agent, controlled with respect to concentration as a solute, for which a definite kinetic order has been firmly established, is the strongly nucleophilic hydroxide ion. It has been shown that the replacement of halogen in the bromo- or chloro-pentamminocobalt(III) ion by hydroxyl, through reaction with alkali hydroxide, is kinetically of the second order (Brönsted and Livingstone, *J. Amer. Chem. Soc.*, 1927, **49**, 435; Puente, *Anal. Asoc. Quim. Argentina*, 1943, **31**, 5),* and therefore we have some grounds for a tentative inference that these are S_N2 reactions, that is, bimolecular nucleophilic substitutions (like the alkaline hydrolysis of methyl chloride):

$$OH^- + [Co(NH_3)_5X]^{++} \longrightarrow [Co(NH_3)_5(OH)]^{++} + X^- \quad . \; . \; . \; . \quad (S_N2)$$

The kinetic evidence is, however, not quite unequivocal, because the same kinetics are required by two other mechanisms, labelled S_N1cB and S_N2cB, that is, unimolecular substitution in the conjugate base of the cobaltammine (as in the alkaline hydrolysis of chloroform), and bimolecular substitution in the conjugate base (some probable examples of such substitution are mentioned below). In the present application of these mechanisms a proton would first be removed from one of the ammonia ligands by the reagent hydroxide ion, and then the conjugate base so produced would lose a halide ion, with the subsequent or simultaneous uptake of the ions of water. Ways are known by which the straightforward mechanism S_N2 can be distinguished from these conjugate-base mechanisms; but they have not yet been applied to the cases discussed.

The reaction which is usually dominating in aqueous solution, even in the presence of some anions, is solvolytic aquation, the kinetics of which have been followed for replacement by water of chloro-, bromo-, and nitrato-groups from the pentamminocobalt(III) ions (Lamb and Marden, *J. Amer. Chem. Soc.*, 1911, **33**, 1873; Brönsted, *Z. physikal. Chem.*, 1926, **122**, 386; Garrick, *Trans. Faraday Soc.*, 1937, **33**, 486; Adell, *Z. anorg. Chem.*, 1941, **246**, 303), of chloro-, bromo-, iodo-, and nitrato-groups from the pentamminoiridium(III) ions (Lamb and Fairhall, *J. Amer. Chem. Soc.*, 1923, **45**, 378), and of chloro-, bromo-, and iodo-groups from the pentamminochromium(III) ions (Freundlich and Bartels, *Z. physikal. Chem.*, 1922, **101**, 177):

$$H_2O + [M(NH_3)_5X]^{++} \longrightarrow [M(NH_3)_5(H_2O)]^{+++} + X^-$$

These are first-order reactions, but this result does not disclose mechanism. Some support may, however, be adduced for the view that the substitutions in the cobalt complexes are bimolecular, with a water molecule as the second reactant; for the rates of displacement of chloro-, bromo-, and nitrato-groups from these complexes are nearly in the same ratios

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* Observed second-order kinetics in the replacement of an acetato- or substituted acetato-group in the appropriate acetatopentamminocobalt(III) ion by a hydroxyl group in reaction with aqueous alkali (Basolo, Bergmann, and Pearson, *J. Phys. Chem.*, 1952, **56**, 22) cannot be accepted as evidence of the kinetics of substitution at cobalt in the absence of a demonstration that the metal–oxygen bond, rather than the acyl–oxygen bond, is broken in this substitution; for the carboxyl mechanism $B_{AC}2$ might here be under observation (cf. Bunton and Llewellyn, forthcoming paper).

for the first-order reactions with solvent water as for the second-order reactions with hydroxide ions. It seems unlikely that the agreement, shown in Table 2, would be so close if the mechanisms differed fundamentally, and the most obvious interpretation is that all these substitutions take place by mechanism S_N2.

TABLE 2. *Rates of displacement of* X *from* $[\text{Co(NH}_3)_5\text{X}]^{++}$ *by water and by hydroxide ions.*

	Rates			Ratios	
X displaced	Cl	Br	NO_3	Cl/Br	Br/NO_3
By H_2O { 10^5k_1, 25°, k_1 in sec.$^{-1}$	0·16	0·65	3·00	4·1	4·6
By H_2O { ,, 15°, ,,	—	0·16	0·60	—	3·8
By OH^- { k_2 in sec.$^{-1}$ mole^{-1} l., 25°	1·30	5·93	—	4·6	—
By OH^- { ,, ,, 15°	—	1·42	5·91	—	4·1

Measurements of the rate of solvolytic displacement by water of chloro- and nitrato-groups from the relevant aquotetrammino- or aquobisethylenediamine-cobalt(III) ions have shown that the substitution goes partly through the conjugate base of the original aquo-compound, as illustrated below, to an extent depending in the expected manner on the pH (Brönsted, *Z. physikal. Chem.*, 1926, **122**, 383; Matsuno, *Bull. Chem. Soc. Japan*, 1926, **1**, 133; Tsuchida, *ibid.*, 1936, **11**, 721; Brüll, *Compt. rend.*, 1936, **202**, 1584; 1937, **204**, 349; Mathieu, *Bull. Soc. chim.*, 1936, **3**, 2121, 2152; 1937, **4**, 687; Ovenston, Thesis, London, 1936):

$$\begin{tikzcd}
{[\text{Co en}_2(\text{H}_2\text{O})\text{Cl}]^{++}} \arrow[r, "S_N2"] \arrow[d] & {[\text{Co en}_2(\text{H}_2\text{O})_2]^{+++}} \\
{[\text{Co en}_2(\text{OH})\text{Cl}]^{+}} \arrow[r, "S_N2\text{cB}"] & {[\text{Co en}_2(\text{OH})(\text{H}_2\text{O})]^{++}} \arrow[u]
\end{tikzcd}$$

There is, however, no indication in these results of a fundamental difference of mechanism of substitution, which we suppose to be bimolecular, that is, S_N2 or S_N2cB as indicated. It is implied that there is no difference in the type of binding of the displaceable ligand in the presence of the aquo-groups.*

(2*b*) *Indications of a Unimolecular Mechanism in Octahedral Substitution.*—That bond type may not be generally retained in the presence of aquo-groups is indicated by observations on the isotopic exchange of ligands and of central metal ions. Ligand exchanges occur at widely different rates in water: the exchange of chloride ion with chlorine in $[\text{Co en}_2\text{Cl}_2]^+$ takes place too slowly to compete with aquation (Ettle and Johnson, *J.*, 1939, 1490), while that of bromide ion with bromine in $[\text{PtBr}_6]^{--}$ occurs too rapidly for measurement (Grinberg, *Bull. Acad. Sci. U.S.S.R.*, 1940, **4**, 342). The chromic ion has been shown, by the use of $H_2{}^{18}O$ to exist in water as $[\text{Cr(H}_2\text{O)}_6]^{+++}$, evidently a covalently bonded complex, since it exchanges its water ligands only slowly. Theory teaches that these covalencies are constructed from d^2sp^3 chromium orbitals. On the other hand, the hydrated ferric ion, $[\text{Fe(H}_2\text{O)}_6]^{+++}$, whose magnetic moment shows that it is not using the orbitals needed to hold the water by similarly constituted bonds, exchanges the water very rapidly (Hunt and Taube, *J. Chem. Phys.*, 1951, **19**, 602). The present approach to the description of such labile bonds is to regard them as formed from sp^3d^2 orbitals, that is, as involving higher d orbitals (4*d* in the example cited), which, by carrying the bonding electrons far from the central nucleus, produce bonds both highly polar and very easily heterolysed (Taube, *Chem. Reviews*, 1952, **50**, 69; Burstall and Nyholm, *J.*, 1952, 3570; Nyholm and Sharpe, *ibid.*, p. 3579; Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, in the press). The ions $[\text{Ni(CN)}_4]^{--}$ and $[\text{Pd(CN)}_4]^{--}$ exchange ligands with labelled cyanide ion too rapidly for measurement, but the ions $[\text{Cr(CN)}_6]^{---}$, $[\text{Co(CN)}_6]^{---}$, $[\text{Fe(CN)}_6]^{---}$, and $[\text{Fe(CN)}_6]^{----}$ do so too slowly, while the ion $[\text{Mn(CN)}_6]^{---}$ undergoes the exchange at a measurable rate, which, significantly, is of zero order with respect to cyanide ion (Adam-

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* Unimolecular aquation of cobalt complexes has been suggested by Pearson, Boston, and Basolo (*J. Amer. Chem. Soc.*, 1952, **74**, 2944), but only on the basis of a much over-simplified discussion of structural effects on reaction rate, a discussion which, in particular, takes no account of polar effects.

son, Welker, and Volpe, *J. Amer. Chem. Soc.*, 1950, **72**, 4030; Adamson, Welker, and Wright, *ibid.*, 1951, **73**, 4786).

In a number of cases, rates of metal-ion exchange appear qualitatively at least to follow those of ligand exchange. Metal exchanges of $[\mathrm{Ni\ en_3}]^{++}$, and some other forms of nickel(II), with $[\mathrm{Ni(CN)_4}]^{--}$ are rapid (Long, *J. Amer. Chem. Soc.*, 1951, **73**, 537), but that of $[\mathrm{Cr(H_2O)_6}]^{+++}$ with $[\mathrm{Cr(CN)_6}]^{---}$ is very slow (Menker and Garner, *ibid.*, 1949, **71**, 371), as is that of $[\mathrm{Co(H_2O)_6}]^{+++}$ with $[\mathrm{Co(NH_3)_6}]^{+++}$ and with $[\mathrm{Co(CN)_6}]^{---}$ (Hoshowsky, Holmes, and McCallum, *Canadian J. Res.*, 1949, **27**, *B*, 258). Exchange between aqueous $\mathrm{Ni^{++}}$ and $[\mathrm{Ni\ dipy_3}]^{++}$, where " dipy " stands for 2 : 2′-dipyridyl, is stated to be nearly complete in 90 min. at room temperature (Johnson and Hall, *J. Amer. Chem. Soc.*, 1948, **70**, 2344), while the optically active dipyridyl complex is reported to racemise in water with a half-life of 15 min. at 17° (Morgan and Burstall, *J.*, 1931, 2213). Exchange of aqueous $\mathrm{Fe^{++}}$ with $[\mathrm{Fe\ dipy_3}]^{++}$ proceeds to the extent of about 25% in 120 min. at room temperature (Ruben, Kamen, Allen, and Nahinsky, *J. Amer. Chem. Soc.*, 1942, **64**, 2297), whereas the half-life for racemisation of the optically active complex in water is recorded as 75 min. at 17·5° (N. R. Davies and F. P. Dwyer, personal communication). The exchange of aqueous $\mathrm{Fe^{++}}$ with $[\mathrm{Fe\ ophen_3}]^{++}$, where " ophen " represents *o*-phenanthroline, has a half-life of 100 min. at room temperature (Ruben *et al.*, *loc. cit.*), while the optically active phenanthroline complex racemises with a half-life of 121 min. at 15° (Davies and Dwyer, personal communication).

The concept of the exchange of central metal ions in a single bimolecular stage is very difficult. The picture which the foregoing observations suggest as applying to certain cases, though probably not in this simple form to all, is that of rate control by a reaction rupturing the first metal–ligand bond, all subsequent stages of breakdown and resynthesis being more rapid. We could then understand why rates of ligand exchange and metal exchange seem often to follow each other, and why a number of rates of racemisation and of exchange of the central metal are of the same order of magnitude. If in aqueous solution the rate-controlling first step involved either a mono-aquation, or the simple heterolysis of one ligand, we could understand how a rate of cyanide exchange could be independent of the concentration of cyanide ions.

Now it is probable that, for some central ions at least, aquation can so change bond-type as to lead to ready heterolysis. We know from magnetic data, as well as from chemical considerations, that $[\mathrm{Fe(CN)_6}]^{---}$ has strong, essentially covalent bonds, formed, it is presumed, with the aid of d^2sp^3 iron orbitals, whereas $[\mathrm{Fe(H_2O)_6}]^{+++}$, which does not contain such bonds, is a structure of covalent, highly polar and therefore very easily heterolysed bonds, formed, as it is believed, with upper-*d*-containing sp^3d^2 orbitals. Therefore, the sequence of substitutions which would convert the former complex ion into the latter, although it doubtless starts with some stages of bimolecular aquation, as would assist displacement of the originally strongly bound ligands, is likely, as the binding becomes more labile and more polar, to end with substitutions resulting from spontaneous heterolysis, that is, with stages of unimolecular aquation. We expect the main changes of bond type to occur together in all the bonds of the central metal, even when two kinds of ligands are being bound, because bond constitutions are linked by orbital occupancy in the central atom, and thus with the numbers of unpaired spins. Moreover, the major changes of bond constitution are likely to occur at some one stage of the series of stages of substitution, because the sharply alternative modes of spin coupling will resist slow gradations. Thus we can reasonably look for a somewhat sudden change, at some stage, from a bimolecular to a unimolecular mode of displacement of the ligands. If our series of substitutions, instead of consisting in the conversion of $[\mathrm{Fe(CN)_6}]^{---}$ into $[\mathrm{Fe(H_2O)_6}]^{+++}$, had consisted in the conversion of $[\mathrm{Fe\ ophen_3}]^{++}$ into $[\mathrm{Fe(H_2O)_6}]^{++}$, then the near-equivalence of the iron exchange rate and the racemisation rate would give reason for thinking that the change of mechanism probably occurs between the first stage of substitution and the second.

What has been said of aqueous iron(II) and iron(III) complexes is probably equally true of nickel(II) complexes, but not of cobalt(III) and chromium(III) complexes. Optically active mono- and di-aquocobalt(III) complexes, *e.g.*, $[\mathrm{Co\ en_2(NO_2)(H_2O)}]^{++}$, $[\mathrm{Co\ en_2Cl(H_2O)}]^{++}$, and $[\mathrm{Co\ en_2(H_2O)_2}]^{+++}$, have been prepared (Werner, *Ber.*, 1911, **44**, 3272; Mathieu, *Bull. Soc. chim.*, 1937, **4**, 687). There is magnetic evidence that $[Co(H_2O)_6]^{+++}$, and isotopic evidence that $[Cr(H_2O)_6]^{+++}$ have strong covalencies. Consistently, cobalt(III) and chromium(III) are among the central metal ions which have not been observed to undergo metal-ion exchange. Thus the stages of successive aquation of complex ions of cobalt and chromium might remain bimolecular to the end (at least, the constitutions of the products do not prove otherwise), whereas those of the complex ions of iron and nickel should go into the unimolecular form as heterolysis of the ligands becomes easier. However, if we should work in a solvent of much smaller complexing power than water, then a switch from the bimolecular to the unimolecular mechanism might occur in the early stages of solvolysis even of cobalt and chromium complexes; and when heterolysis of the ligands occurs sufficiently readily, then non-solvolytic substitutions, as by weakly nucleophilic anions, could be unimolecular. In planning work based on Werner's, it is natural to think first of the aqueous reactions of cobalt ions; but whether we then widen the field by including other metals, or by going over to other solvents, the above survey suggests that we must expect to encounter both the bimolecular and the unimolecular mechanisms of substitution—S_N2 and S_N1—and perhaps intermediate, or even quite different mechanisms also.

Actually we have commenced our experimental study by using cobalt complexes. However, we have employed as solvent, not only water, as when strongly nucleophilic reagents were under examination, but also, and extensively, the very much more feebly complexing solvent, methyl alcohol, the purpose being to repress solvolytic substitution when a weakly nucleophilic solute was the intended reagent. Within this range of experience, we do indeed find both the standard mechanisms of substitution; and our survey suggests that we should accept this finding as typical for octahedral substitutions in general.

William Ramsay and Ralph Forster Laboratories,
University College, Gower St., London, W.C.1.

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