QUARTERLY REVIEWS

THE STABILITIES OF COMPLEX COMPOUNDS

By A. R. Burkin, M.Sc., Ph.D., F.R.I.C.
(University College, Southampton)

For many years workers in the field of co-ordination chemistry were concerned almost exclusively with the stereochemistry of complexes and with the preparation of complexes of new types or containing new ligands (or co-ordinating groups). The nature of the forces involved between the metal ion and the co-ordinating atom was also a problem which attracted a number of workers, and the present situation has been reviewed by Nyholm.[1]

Until fairly recently the physicochemical principles involved in complex formation had received scant attention, and there was little quantitative information available to show the influence of the ligand on the properties of the complexes formed by a particular metal, or how the properties of complexes containing the same ligand depended on the position of the metal in the Periodic Table. The aim of this Review is to present a concise picture of the present state of our knowledge of these factors and to show the importance of a fuller understanding of them.

The properties of the complex compounds of a metal are not usually regarded as being typical of the metal in the same way as are those of the insoluble compounds and simple salts. This is probably due to the influence of the ligand on the properties of complexes. In aqueous solution, however, metal ions are invariably hydrated, and in many cases it is to be supposed that water molecules are co-ordinated to the ion to give aquo-complexes analogous to the ammines and other typical co-ordination compounds. In a number of cases, involving the metals whose salts are hydrolysed in solution, hydroxo-complexes, where OH^- groups are co-ordinated, or possibly even oxo-complexes, containing O^{--} ions, may be formed. These usually polymerise and may finally give colloidal solutions of the metal hydroxide. Anions which are present also co-ordinate, and in acid solutions, where hydrolysis is prevented, considerable numbers of anions may be attached to the metal ions. In the cases of some metals, particularly those of the platinum group, simple solvated ions are never formed, and the chemistry of such metals is essentially the chemistry of their complex compounds.

Complex formation affects the properties of the metal ions, often very considerably. In extreme cases, such as the formation of $[Fe(CN)_6]^{----}$

---

[1] *Quart. Reviews*, 1949, **3**, 321.

ions, the reactions of the metal normally regarded as "characteristic" can no longer be detected. Many physical properties of a metal ion are altered by co-ordination, *e.g.*, the deposition potential, colour, and extinction coefficient. A solution of the metal salt in water may, therefore, be unsuitable for any purpose requiring a knowledge of such a property, since a number of complex species involving anions, hydroxo-groups, and water molecules will often be present, the relative proportions depending on concentration, the presence of other ions, method of preparation of the solution, temperature, and so on. This difficulty is usually overcome by including in the solution a substance which is a more powerful co-ordinating agent for the metal than is water. If the pH is kept constant, the solution will contain a few complex species in definite proportions depending on their equilibrium constants (see later).

In analytical procedures, interfering metals are often "masked" by adding ions such as F^-, PO_4^{---}, CN^-, etc. Hydroxy-acids like citric or tartaric acid are also commonly used to hold Fe^{+++}, Al^{+++}, Cu^{++}, etc., ions in solution, and there are innumerable other examples. Particularly interesting are the derivatives of iminodiacetic acid, $NH(CH_2{\cdot}CO_2H)_2$, known as "complexones".[2] Masking agents act by virtue of the complexes which they form with the metal ion they hold back, these being more stable than the compound formed between the interfering metal and the reagent added in order to determine the metal required.

The effect of complex formation on the oxidation–reduction potential of a couple containing a metal in two valency states is often pronounced and is frequently of great practical importance. In extreme cases co-ordination may stabilise a valency state not normally found in simple compounds of the metal concerned. Cobalt is a very well-known example where this occurs. Simple salts of tervalent cobalt are unstable whereas complexes of bivalent cobalt, with ammonia for example, are very easily oxidised to the tervalent condition. The situation is expressed quantitatively by the following figures :

Couple.	Potential, volts.
$[Co(H_2O)_x]^{++} = [Co(H_2O)_x]^{+++} + e^-$	$E^\circ = -1{\cdot}842$
$[Co(NH_3)_6]^{++} = [Co(NH_3)_6]^{+++} + e^-$	$E^\circ = -0{\cdot}1$
$[Co(CN)_6]^{----} = [Co(CN)_6]^{---} + e^-$	$E^\circ = +0{\cdot}83$

As these data indicate, the "simple" or hydrated cobaltic ion is a very powerful oxidising agent ; in high concentrations it liberates oxygen rapidly from water. In the hexammine ion the cobaltic state has been considerably stabilised and the process is carried further in the complex cyanides, that of bivalent cobalt being such a powerful reducing agent that it liberates hydrogen from water.

This is a very striking but rather unusual example, and in general the effect of co-ordination on the value of E° is less than this, but many examples of the stabilisation of valencies are known.[3] Applications of this method

---

[2] Cf. Irving, *Ann. Reports*, 1949, **46**, 273.

[3] Copley, Foster, and Bailar, jnr., *Chem. Reviews*, 1942, **30**, 227.

of controlling E° are numerous in both pure and applied chemistry, and it would be extremely valuable if ligands could be found to give any particular value of E° required. This would involve a quantitative knowledge of all the factors involved, and such a situation is remote. However, work on the oxidation–reduction potentials of the complexes of substituted 1 : 10-phenanthrolines with ferrous and ferric iron has shown regularities in the effects of substituents so that the complexes can be used as indicators in redox titrations over the range 1·10—0·84 v.[4]

The properties of complexes are of considerable importance in the separation of metals by base-exchange resins (*e.g.*, large quantities of pure rare-earth metal compounds can be obtained by this method [5]). In this case the important property is the pH at which the complex decomposes to give metal ions capable of being adsorbed on the resin.[6]

The most important measurable quantity concerned in any theory intended to explain and correlate the phenomena concerned with complex formation is the stability constant of the complex. A metal ion M^{x+} and a monodentate neutral ligand A (*i.e.*, a non-ionic ligand each molecule of which occupies only one co-ordination position around the metal ion) will give as the final complex ion formed, either $[MA_4]^{x+}$ or $[MA_6]^{x+}$, depending on whether the co-ordination number N of the metal is 4 or 6. Some metals have other values of N, such as 2 or 8, and polynuclear complexes may be formed, but we need not consider such cases here. If A were an ion, then the charge on the complex ion would depend on the value of x, the ionic charge on A, and the number of A groups attached. The overall reaction is reversible and may be written :

$$M^{x+} + NA \rightleftharpoons [MA_N]^{x+}$$

and the overall equilibrium constant K_N will be given by

$$K_N = [MA_N{}^{x+}]/[M^{x+}][A]^N$$

square brackets here representing concentrations. It is assumed that the activities of the reacting groups are equal to the concentrations, and the experimental conditions are chosen so that this is approximately the case, low concentrations of the reactants being used in the presence of a highly dissociated neutral salt.

From the value of K_N may be calculated the standard free energy ΔG° and the standard potential E° for the reaction, by means of the usual relationships :

$$\Delta G^\circ = -\boldsymbol{R}T \ln K_N \; ; \quad E^\circ = (\boldsymbol{R}T/n\boldsymbol{F}) \ln K_N$$

At 25°, we have

$$\Delta G^\circ \text{ (cals.)} = -1364{\cdot}0 \log_{10} K_N \; ; \qquad E^\circ \text{ (volts)} = (0{\cdot}05914/n) \log_{10} K_N$$

In the case of oxidation–reduction equilibria the situation may be generalised as follows. Let the reaction be

$$[MA_N]^{x+} + H^+_{aq.} \rightleftharpoons [MA_N]^{(x+1)+} + \tfrac{1}{2}H_2 \quad . \quad . \quad (1)$$

---

[4] Brandt and Smith, *Analyt. Chem.*, 1949, **21**, 1313.

[5] Spedding, *Discuss. Faraday Soc.*, 1949, **7**, 214.

[6] Duncan and Lister, *Quart. Reviews*, 1948, **2**, 338.

which is equivalent to the reaction of the cobaltocyanide ion $[Co(CN)_6]^{----}$ in acid solution to give cobalticyanide ion $[Co(CN)_6]^{---}$ and hydrogen. Equation (1) may be broken into steps as follows :

$$M^{x+}_{gas} \longrightarrow [MA_N]^{x+}_{gas} \quad . \quad . \quad . \quad . \quad (2)$$
$$M^{x+}_{gas} \longrightarrow M^{(x+1)+}_{gas} + e^- \quad . \quad . \quad . \quad (3)$$
$$M^{(x+1)+}_{gas} \longrightarrow [MA_N]^{(x+1)+}_{gas} \quad . \quad . \quad . \quad . \quad (4)$$
$$H^+_{aq.} \longrightarrow H^+_{gas} \quad . \quad . \quad . \quad . \quad . \quad (5)$$
$$H^+_{gas} + e^- \longrightarrow H_{gas} \quad . \quad . \quad . \quad . \quad . \quad (6)$$
$$H_{gas} \longrightarrow \tfrac{1}{2}H_2 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Solvation energies of the complex ions are considered later.

The free energy of reaction (1) is

$$\Delta G_1 = -\Delta G_2 + \Delta G_3 + \Delta G_4 + \Delta G_5 + \Delta G_6 + \Delta G_7$$

which may be re-written as

$$\Delta G_1 = -\Delta G_2 + I + \Delta G_4 + \Delta G_5 - I_H + \Delta G_7$$

where I and I_H are the ionisation potentials of the gaseous metal ion M^{x+} and of the gaseous hydrogen ion, respectively.

For standard conditions

$$\Delta G_1^\circ = -\Delta G_2^\circ + \Delta G_4^\circ + I + A$$

where the term A is a constant and in this case is connected with the properties of the hydrogen ion, used as oxidising agent. Hence the standard oxidation–reduction potential, E_1°, of the reaction may be calculated directly. Any other oxidising agent could be used, which would change the value of E° for the reaction, but have no effect on the value of E_8° for the couple in which we are primarily interested, namely

$$[MA_N]^{x+} = [MA_N]^{(x+1)+} + e^- \quad . \quad . \quad . \quad . \quad (8)$$

For this we may write $\Delta G_8^\circ = \Delta G_4^\circ - \Delta G_2^\circ + I$. It is now obvious that E_8° depends on (*a*) the value of I, which is a characteristic of the metal ion concerned and is unaffected by co-ordination of other groups, (*b*) the free energy of the reaction (2), and (*c*) the free energy of reaction (4).

In practice, ΔG_2 and ΔG_4 cannot be determined directly from equilibrium data since the experiments must be carried out in aqueous solution. Each system must then be divided into two steps, thus for ΔG_2

$$M^{x+}_{gas} \longrightarrow M^{x+}_{aq.} \quad . \quad . \quad . \quad . \quad . \quad (9)$$
$$M^{x+}_{aq.} + NA \longrightarrow [MA_N]^{x+} + aq. \quad . \quad . \quad . \quad (10)$$

The equilibrium constant determined is that for (10) and is a measure of the work done when N groups of ligand A replace the water present in the hydrated metal ion. The value of E_8°, therefore, depends not only on the measured equilibrium constants for the complex ions, but also on the energies of solvation of the metal ions in the two valency states. For comparative purposes, using a single metal, however, only the equilibrium constants need be considered.

Stability and Bond Strength

It is useful in problems in theoretical chemistry to consider bond strengths, and the stability constant of a complex species is obviously related to the strength of the metal–ligand bond. The changes in free energy, ΔG, heat of formation, ΔH, and entropy, ΔS, are connected by the relationship $\Delta G = \Delta H - T\Delta S$, where T is the temperature, and, if the entropy change on complex formation, or replacement of water by ligand groups, is small, then $RT \ln K$ may be used as a measure of the bond strength. If, however, ΔS is not small, this is not justified.

The simplest method of determining ΔS is by obtaining values of K at different temperatures, but this has not been done in the past except in a few cases. Such measurements as have been made, however, give an indication of the conditions under which ΔS may not be small enough to be ignored.

Calvin and Bailes[7] found the accompanying values of ΔH and ΔS for the following systems :

$$\mathrm{Ni^{++}(H_2O)}_x + 6\mathrm{NH_{3_{aq.}}} \rightleftharpoons \mathrm{Ni(NH_3)_{6_{aq.}}^{++}} + x\mathrm{H_2O} \quad \begin{cases} \Delta H \triangleq -\ 19 \text{ kcals.} \\ \Delta S \triangleq -\ 22 \text{ cals./deg.} \end{cases}$$

$$\mathrm{Ni^{++}(H_2O)}_x + 3\mathrm{en_{aq.}} \rightleftharpoons \mathrm{Ni\,en_{3_{aq.}}^{++}} + x\mathrm{H_2O} \quad \begin{cases} \Delta H \triangleq -\ 25 \text{ kcals.} \\ \Delta S \triangleq +\ 2 \text{ cals./deg.} \end{cases}$$

and hence calculated the following values for replacement of ammonia by ethylenediamine :

$$\mathrm{Ni(NH_3)_6^{++}} + 3\mathrm{en_{aq.}} \rightleftharpoons \mathrm{Ni\,en_3^{++}} + 6\mathrm{NH_{3_{aq.}}} \quad \begin{cases} \Delta H \triangleq -\ 6 \text{ kcals.} \\ \Delta S \triangleq +\ 24 \text{ cals./deg.} \end{cases}$$

In these reactions en represents an ethylenediamine molecule, which behaves as a bidentate chelating group since both amino-groups can co-ordinate to the metal.

The authors point out that the third system indicates the entropy increase caused by increasing the number of particles present. A comparison of the first two reactions shows the gain in configurational entropy on forming a ring system by chelation, a factor of major importance since it is one of the main reasons for the relatively greater stabilities of complex compounds containing polydentate ligands compared with those of complexes of monodentate substances.[8]

Removal of ionic charges from the system by complex formation also causes a large increase in the entropy of the solvent because the ordered arrangement of the solvent around ions is lost. This is shown by the following data given by Rabinowitch and Stockmayer :[9]

$$\mathrm{Fe_{aq.}^{+++}} + \mathrm{Cl_{aq.}^{-}} \rightleftharpoons \mathrm{FeCl_{aq.}^{++}} \qquad \Delta S \sim +\ 35 \text{ cals./deg.}$$

$$\mathrm{Fe_{aq.}^{+++}} + \mathrm{Br_{aq.}^{-}} \rightleftharpoons \mathrm{FeBr_{aq.}^{++}} \qquad \Delta S \sim +\ 23 \text{ cals./deg.}$$

$$\mathrm{Fe_{aq.}^{+++}} + \mathrm{OH_{aq.}^{-}} \rightleftharpoons \mathrm{FeOH_{aq.}^{++}} \qquad \Delta S \sim +\ 50 \text{ cals./deg.}$$

The effect of chelate formation and simultaneous removal of ionic

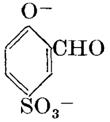
---

[7] *J. Amer. Chem. Soc.*, 1946, **68**, 949.

[8] Irving and Williams, *Nature*, 1948, **162**, 746.

[9] *J. Amer. Chem. Soc.*, 1942, **64**, 335.

charges is shown by the following figures for the formation of the cupric complex of the salicylaldehyde-5-sulphonate ion (A) in (I).[10] This behaves



(I.)

as a bidentate ligand, the sulphonate ion taking no part in complex formation :

$$\mathrm{Cu^{++}(H_2O)}_x + 2\mathrm{A^{--}(H_2O)}_{2_{\mathrm{aq.}}} \rightleftharpoons \mathrm{CuA}_{2_{\mathrm{aq.}}}^{--} + y\mathrm{H_2O} \quad \begin{cases} \Delta H \sim +17 \text{ kcals.} \\ \Delta S \sim +100 \text{ cals./deg.} \end{cases}$$

The number of particles in the system is also increased most probably, since after complex formation only one ion is present, compared with the three before reaction, and less water is required for solvation.

It is to be hoped that, in future, values of ΔS° will be measured at the same time as equilibrium constants, but in order to use existing data it is usually assumed that, for similar systems, differences in ΔS° will be small and that values of ΔG° can be used as a measure of metal–ligand bond strengths. However, the limitations of this assumption must always be remembered.

Successive Equilibrium Constants

Work carried out by Abegg, Bodlander, and others, at the beginning of this century, was concerned with determining the overall equilibrium constant $K_N = [\mathrm{MA}_N]/[\mathrm{M}][\mathrm{A}]^N$ for the complex MA_N. Later work has shown that addition of a ligand to a metal ion always proceeds step-wise and a series of stability constants can be obtained. Considering the formation of a complex MA_4 and ignoring the fact that all components will be hydrated, we have, if A is a neutral monodentate ligand :

$$\begin{array}{lcll} \mathrm{M}^{x+} + \mathrm{A} & \rightleftharpoons & \mathrm{MA}^{x+} & k_1 = [\mathrm{MA}^{x+}]/[\mathrm{M}^{x+}][\mathrm{A}] \\ \cdots & \cdots & \cdots & \cdots \\ \mathrm{MA}_3{}^{x+} + \mathrm{A} & \rightleftharpoons & \mathrm{MA}_4{}^{x+} & k_4 = [\mathrm{MA}_4{}^{x+}]/[\mathrm{MA}_3{}^{x+}][\mathrm{A}] \end{array}$$

and $K_4 = k_1k_2k_3k_4$. The essential questions which arise are what factors influence (*a*) the absolute values, and (*b*) the relative values of the successive constants ?

It is convenient to consider the second of these points first in the terminology of J. Bjerrum.[11] The logarithm of the ratio of two consecutive constants is called the " total effect ", $T_{n,n+1}$

$$\log k_n/k_{n+1} = T_{n,n+1}$$

and this may be subdivided into two quantities, the " statistical effect ", $S_{n,n+1}$, and the " ligand effect ", $L_{n,n+1}$:

$$T_{n,n+1} = S_{n,n+1} + L_{n,n+1}$$

Statistical Effect.—The statistical effect is due to the fact that if the

---

[10] Calvin and Melchior, *J. Amer. Chem. Soc.*, 1948, **70**, 3270.

[11] " Metal Ammine Formation in Aqueous Solution ", P. Haase & Son, Copenhagen, 1941.

total number of ligand molecules bound to the metal atom in the highest complex formed is N, then the magnitude of the successive complexity constants will be affected by the number n of ligand molecules already present in the complex. It is usually postulated that the tendency in a complex MA_n to split off one group A is proportional to n, and its tendency to take up another ligand group is proportional to $N - n$. The N consecutive complexity constants will then be proportional to

$$\frac{N}{1}, \frac{N-1}{2}, \ldots \frac{N-n+1}{n}, \frac{N-n}{n+1}, \ldots \frac{2}{N-1}, \frac{1}{N}$$

so that the ratio between two consecutive constants due to statistical causes alone is given by

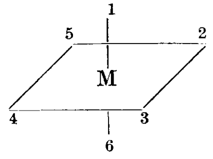
$$\frac{k_n}{k_{n+1}} = \frac{(N-n+1)(n+1)}{(N-n)n}$$

Therefore

$$S_{n,n+1} = \log k_n - \log k_{n+1} = \log \frac{(N-n+1)(n+1)}{(N-n)n}$$

This expression will apply if each ligand group A occupies only one co-ordination position and if the N co-ordination positions around the metal atom are identical.

For bidentate groups which possess two groups able to attach themselves to the metal atom and so occupy two co-ordination positions, *e.g.*, ethylenediamine, the expression for the statistical effect has to be modified. The number Z of bidentate ligands which can be bound is $N/2$, and it is possible to introduce the $(n + 1)$th ligand group into the molecule in more than $Z - n$ ways. Consider as an example a 6-covalent metal ion, in which the six co-ordination positions are situated at the corners of a regular octahedron, as in the diagram (inset). Each position is equivalent so long as none is occupied. Three symmetrical bidentate ligand groups are to be introduced ($Z = 3$). The first group can arrange itself in twelve ways and let us suppose that it occupies positions 1 and 2. The second group can then arrange itself in five ways, occupying the 6,3 ; 6,4 ; 6,5 ; 3,4 ; or 4,5 corners. A bidentate ligand can never occupy two positions which are *trans* to one another, so the group cannot occupy the 3,5 position. Since the tendency of a ligand group to split off is proportional to the number of ligand groups in the complex, the first two consecutive constants will have a ratio proportional to the ratio of the fractions $\frac{12}{1} : \frac{5}{2}$. The third ligand group can arrange itself in only one way, but if the second group took up the 6,4 position, leaving corners 3 and 5 vacant, then the third group cannot attach itself at all, and its relative tendency to attach itself, which would otherwise be $\frac{1}{3}$, must be modified by the factor $\frac{4}{5}$ since in only four out of five cases can it be attached at all. The ratio of the three constants will be $\frac{12}{1} : \frac{5}{2} : \frac{4}{15}$, so that $S_{1,2} = \log \frac{12}{1} \div \frac{5}{2} = 0{\cdot}681$, and $S_{2,3} = 0{\cdot}972$.



The statistical effect, which makes $k_n > k_{n+1}$, may overshadow effects on the relative values of k_n and k_{n+1} owing to other causes. It is sometimes important, therefore, to be able to correct the experimentally determined constants for the statistical effect, and the following example shows the method adopted.

Consider the system $Cr^{+++} + 6SCN^-$, the consecutive constants of which were found experimentally[12] to be

$\log k_1$	$\log k_2$	$\log k_3$	$\log k_4$	$\log k_5$	$\log k_6$
3·1	1·7	1·0	0·3	− 0·7	− 1·6

The statistical corrections calculated for $N = 6$ are

$$S_{1,2} = S_{5,6} = 0{\cdot}4\ ;\quad S_{2,3} = S_{4,5} = 0{\cdot}3\ ;\quad S_{3,4} = 0{\cdot}2$$

Let the corrected values of $k_1 \ldots k_6$ be a, b, c, d, e, f. Then $\log k_1/k_2 = \log k_1 - \log k_2 = 1{\cdot}4$, but this value is too high by an amount equal to $S_{1,2}$, so that the difference between the corrected values, $a - b$, must be given by

$$a - b = 1{\cdot}4 - 0{\cdot}4 = 1{\cdot}0$$

Similarly

$$b - c = 0{\cdot}7 - 0{\cdot}3 = 0{\cdot}4 \qquad d - e = 1{\cdot}0 - 0{\cdot}3 = 0{\cdot}7$$
$$c - d = 0{\cdot}7 - 0{\cdot}2 = 0{\cdot}5 \qquad e - f = 0{\cdot}9 - 0{\cdot}4 = 0{\cdot}5$$

The individual corrected constants are now calculated by making the logarithm of the mean complexity constant, defined by

$$\log k_{\text{av.}} = \frac{1}{N}\log K_N = \frac{1}{N}\log k_1 k_2 \ . \ . \ . \ k_N$$

have the same value when calculated from the statistically corrected constants as from the experimental constants. Therefore,

$$\log k_{\text{av.}} = 3{\cdot}8/6 \quad \text{and} \quad a + b + c + d + e + f = 3{\cdot}8.$$

By simple substitution the values of $a \ldots f$ are found to be

$n =$	1	2	3	4	5	6
$\log k_n$ (corr.) =	2·3	1·3	0·9	0·4	− 0·3	− 0·8

These values show how the addition of SCN^- groups modifies the ability of the metal to bind further SCN^- groups, giving a measure of the ligand effect

$$L_{n,n+1} = \log k_n \text{ (corr.)} - \log k_{n+1} \text{ (corr.)}$$

Successive constants which have been corrected for the statistical effect are important in so far as they show clearly any abnormal effect on the overall equilibrium constant due to the ligand. The relative values of k_1, k_2, and k_3 for the $Cd^{++} + 4I^-$ system (see table), for example, show that k_2 is far too small, implying that specific factors, so far unexplained, come into play. In this case the effect is so large that there is no need to apply corrections for the statistical effect to see it, but in some cases this is necessary. These other effects are incorporated in the " ligand effect ".

The method used for correcting for the statistical effect does not affect the overall value of the equilibrium constant. The average energy of

---

[12] N. Bjerrum, *Z. anorg. Chem.*, 1921, **118**, 179.

formation of each metal–ligand bond, derived from the mean constant $k_{\text{av.}}$ defined by the relationship

$$\log k_{\text{av.}} = (\log k_1 + \log k_2 \; . \; . \; . \; + \log k_N)/N$$

is, therefore, not affected by the correction.

The Ligand Effect.—The ligand effect may be further subdivided into an "electrostatic" effect, $E_{n,n+1}$, and a "rest" effect, $R_{n,n+1}$:

$$L_{n,n+1} = E_{n,n+1} + R_{n,n+1}$$

The Electrostatic Effect.—The electrostatic effect represents the effect on $\log k_n/k_{n+1}$ of any ionic charge on the ligand. In the case just considered, the chromithiocyanates, addition of the first SCN^- group is helped by the triple positive charge on the metal ion, but the fifth and the sixth SCN^- group have to co-ordinate to an ion which is already negatively charged. Factors such as this will obviously affect the relative values of successive constants, and the magnitude of the electrostatic effect was shown by N. Bjerrum[13] to be represented by

$$E_{n,n+1} = 0{\cdot}4343\phi_{n,n+1}/\boldsymbol{k}T$$

where $\boldsymbol{k}$ represents the Boltzmann constant and $\phi_{n,n+1}$ denotes the work necessary to bring an electrically charged ligand A up to a complex MA_n to give MA_{n+1}. Attempts have been made when dealing with the successive ionisation constants of polyvalent acids to include in the electrostatic effect all polarisation effects, but it is better when dealing with co-ordination systems to limit the electrostatic effect to include only the coulombic forces. Thus the following relationship holds :

Consecutive equilibrium constants of certain systems

System.*	$\log k_1$.	$\log k_2$.	$\log k_3$.	$\log k_4$.	$\log k_5$.	$\log k_6$.	$\log k_{\text{av.}}$	*Z*.	*N*.	Temp.	Ref.
$Cu^{++} + 5NH_3$	4·15	3·50	2·89	2·13	− 0·52		3·17	4	4	30°	14
$Hg^{++} + 4NH_3$	8·8	8·7	1·00	0·78			8·75	2	2	22	14
$Ni^{++} + 6NH_3$	2·80	2·24	1·73	1·19	0·75	0·03	1·46	6	6	30	14
$Cd^{++} + 6NH_3$	2·65	2·10	1·44	0·93	− 0·32	− 1·66	1·78	4	4	30	14
$Cd^{++} + 4I^-$	2·08	0·77	2·15	1·48			1·62	4	4	25	15
$Ag^+ + 2NH_3$	3·20	3·83					3·52	2	2	30	14
Ni^{++} + 3en	7·66	6·40	4·55				6·20	3	6	30	14
Cu^{++} + 3en	10·72	9·31	− 1·0				10·02	2	4	25	16
Cu^{++} + 2den	16·0	5·0					10·5	1—2	4	20	17
Cu^{++} + 2ptn	11·1	9·0					10·1	2	4	20	17
Cu^{++} + 2Hptn	8·8	7·3					8·1	2	4	20	17
Cu^{++} + tren	18·8						18·8	1	4	20	17
Cu^{++} + trien	20·5						20·5	1	4	20	17

* den = diethylenetriamine ; ptn = 1 : 2 : 3-triaminopropane ; Hptn = ion of latter ; tren = triaminotriethylamine ; trien = triethylenetetramine (see p. 11).

$$\phi_{n,n+1} = \boldsymbol{e}^2/Dr$$

where $\boldsymbol{e}$ is the electronic charge, D the dielectric constant of the medium,

---

[13] *Z. physikal. Chem.*, 1923, **106**, 238.

[14] J. Bjerrum, *op. cit.*

[15] Leden, *Z. physikal. Chem.*, 1941, **188**, *A*, 160.

[16] J. Bjerrum and Nielsen, *Acta Chem. Scand.*, 1948, **2**, 297 ; cf. Carlson, McReynolds, and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1334.

[17] Schwarzenbach and Prue, *Helv. Chim. Acta*, 1950, **33**, 947, 963, 974, 985, 995.

and r the distance between the charges. In this way the electrostatic effect in systems where the ligand is non-ionic is made zero by definition.[11]

Rest Effect.—The " rest " effect shows how the properties of the ligand molecule affect the ability of further ligand molecules to attach themselves to the lower complex already formed. In order to avoid difficulties due to the unavoidable uncertainties encountered when trying to calculate the electrostatic effect, it is usual to consider neutral ligands. In the table some constants for consecutive equilibria are given and a number of interesting points appear.

The system Cu^{++}–NH_3 is of some importance since, although the co-ordination number of cupric ions is known to be four, it is possible to measure five successive constants. The first four of these are of the same order of magnitude, and correction for the statistical factor gives the following values which are even closer :

$\log k_1$ (corr.)	3·55	$\log k_2$ (corr.)	3·32
$\log k_3$ (corr.)	3·07	$\log k_4$ (corr.)	2·73

Most of the difference between the first four experimental values is, therefore, due to statistical causes, but the fifth constant is very much smaller. The symbol Z gives the number of uniformly bound ligand molecules, whereas N is the co-ordination number of the metal. For a monodentate ligand, $N = Z$; for a bidentate substance $N = 2Z$, and so on.

A similar situation is found in the complex ammines of cadmium, only here six consecutive constants can be determined, k_5 and k_6 both being very small in comparison with the first four. That $N = 4$ is confirmed by the observation that only four steps can be found in the Cd^{++}–I^- system, the final complex being the $[CdI_4]^{--}$ ion. Here the trend of the successive constants cannot be explained in terms of the electrostatic and statistical effects since these require that $k_n > k_{n+1}$, whereas k_2 is abnormally small and k_3 abnormally large, being in fact greater than k_1. In such cases there must be specific chemical factors coming into play, the nature of which is not fully understood. Irving[18] suggests that some of these anomalies, *e.g.*, that occurring in Ag–NH_3 (and Ag–amine) systems, can be explained in terms of a change in the electron orbitals used for bond formation on passing from one complex to the next.

Polydentate Ligands.—When dealing with bidentate ligands such as ethylenediamine (en), we have $N = 2Z$. The figures for the Cu^{++}–en and Ni^{++}–en systems show that, as expected, $k_n > k_{n+1}$ except when the normal value of N is exceeded. It is important to note, however, that the values of k are very much greater than for the ammonia complexes, and the reasons for this will be considered.

It is to be supposed that the bidentate molecule first attaches itself to one co-ordination position and that the second co-ordinating group then occupies the second position. The two stages of this mechanism are not resolved experimentally, and the value of k_1 gives the free energy for the co-ordination of both groups, so that k_1 for a bidentate ligand must

[18] Private communication.

be compared with ($k_1 \times k_2$) for a monodentate ligand. Similarly, k_2 for the bidentate ligand measures the free energy for the co-ordination of the second bidentate group and must be compared with ($k_3 \times k_4$) for the monodentate ligand.

Even so, it is obvious in the examples mentioned that the ethylenediamine molecules are bound more firmly than ammonia to copper or to nickel and further factors are involved. Since values of k are measured at equilibrium conditions, we may consider what happens when a complex dissociates. An ionically neutral monodentate ligand molecule is free to migrate once it is split off, whereas if one group of the bidentate ligand is freed, the second group holds it in the vicinity of that metal ion so that it is much more readily re-attached than is the monodentate molecule. Alternatively, we may consider the formation of the complex. Once the first group of the bidentate molecule is bound, the activity of the second group with reference to its reaction with the metal ion is greatly increased. Finally, it must be remembered that at equivalent molar concentrations the bidentate ligand, having two reactive groups, is statistically more liable to co-ordinate than a monodentate ligand. The situation may be represented as follows :

$$\log k_{1\ \text{(bidentate ligand)}} = 2 \log k_{1\ \text{(monodentate ligand)}} + \text{statistical factor} + \log \text{activity of free group in bound ligand.}$$

This ignores the fact that in order to fill two co-ordination positions the ligand molecule may be subjected to strain, so that a term should be subtracted to compensate for this. It is noteworthy that in the series of complexes formed by the aliphatic diamines and dicarboxylic acids the stabilities decrease as the number of CH_2 groups between the two active groups increases. This may be attributed, partly at least, to the decrease in the effective activity of the second group after the other is bound, owing to its increased distance from the metal atom.

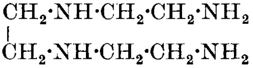
The stability constants of the polyamine–metal complexes are interesting in that they show how the number of active groups in each molecule of ligand and the steric factors influence the equilibrium constants. Figures for the copper complexes are given in the table, and Schwarzenbach [19] has discussed them in some detail. The polyamines used were diethylenetriamine (II), 1 : 2 : 3-triaminopropane (III), and its ion (IV), triaminotriethylamine (V), and triethylenetetramine (VI).

$NH(CH_2{\cdot}CH_2{\cdot}NH_2)_2$
(II.)

$NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2$
(III.)

$^{+}NH_3{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2$
(IV.)

$N(CH_2{\cdot}CH_2{\cdot}NH_2)_3$
(V.)



$$\begin{array}{l} CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2 \\ | \\ CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2 \end{array}$$

(VI.)

Log k_1 for the formation of [Cu den]$^{++}$ is $\frac{3}{2}$ log k_1 for [Cu en]$^{++}$, and it is concluded that all three nitrogen atoms of the triamine co-ordinate,

---

[19] *Angew. Chem.*, 1950, **62**, 218.

each with about the same energy as those of ethylenediamine. The value of k_2 for the diethylenetriamine complex is approximately what would be expected for one further amino-group co-ordinating to fill the fourth co-ordination position around the copper ion.

The first molecule of triaminopropane gives a value for k_1 approximately equal only to the value for ethylenediamine, and the values of k_2 are, similarly, quite close. Hence, it may be concluded that the triamine is behaving as a bidentate ligand. This difference in behaviour between diethylenetriamine and triaminopropane is readily explained, since, whereas the three nitrogen atoms of the former can readily occupy three corners of a square around the copper ion, triaminopropane cannot bend in order to do so, and therefore can act only as a bidentate ligand. In acid solutions the free amino-group will take up a proton, and the lower values of k_1 and k_2 for the resulting Cu^{++}–Hptn system as compared with the values for the free base are obviously due to the repulsive effect of the charges on the ligand and metal ions, to the statistical reduction in the number of free co-ordinating groups, and to a possible entropy factor.

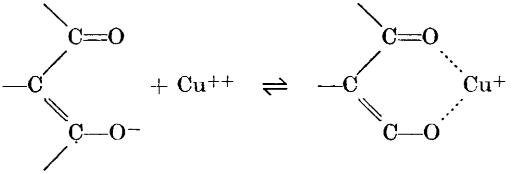
In the cases of the two tetramines only one ligand molecule is attached to the copper ion, and again it is found that, whereas all four nitrogen atoms of triethylenetetramine can co-ordinate, only three of those of triaminotriethylamine can do so, the fourth co-ordination position presumably being occupied by a water molecule. Accordingly, the values of k_1 show the former to be bound more firmly than the latter. It should be noted that Schwarzenbach determined the k values at only one temperature, and in the discussion it is assumed that ΔS° values are small. This may not be justifiable when comparing ligands with different numbers of co-ordinating groups but it is probable that the main conclusions are essentially correct.

The extremely large values of the equilibrium constants found for these polydentate ligands are of great importance. Most metals, including those of the alkali and alkaline-earth series, form rather stable bonds when carboxylic acid groups co-ordinate to them. Extremely stable complexes are formed if amino-polycarboxylic acids such as ethylenediaminetetra-acetic acid or the aminophosphoric acids are used as co-ordinating agents since these behave in a manner exactly analogous to the polyamines. Accordingly, it is possible to titrate metal ions with such " complexones " in just the same way as hydrogen ions can be titrated with alkali, and metal ions may also be buffered. Certain organic dyes behave as co-ordinating groups and some of them change colour on forming complexes, and may, therefore, be used as indicators. The modern method of determining the hardness of water is an application of this type of method. Ethylenediaminetetra-acetic acid is used as complexing agent and, *e.g.*, Eriochrome Black T, as indicator. Alkaline-earth metal complexes of the dye are reddish-mauve, but the disodium salt is blue, so when the last trace of alkaline-earth metal is extracted during titration with standard ethylenediaminetetra-acetic acid solution, the colour change is sharp. A suitable pH has, of course, to be maintained by buffering the solution.

The redox potentials of many metal–ion couples are modified considerably by complex formation with polydentate ligands since the complexes are extremely stable. The normal potential of 1·8 v. for the hydrated Co^{+++}–Co^{++} system is reduced to about 0·6 v. by complex formation with ethylenediaminetetra-acetic acid, the exact value depending on the pH. Under these conditions, therefore, ceric sulphate can be used for the oxidation of the bivalent cobalt, giving a volumetric method for this metal.[20]

Ligand Basicity.—The formal analogy between metal–ligand and protein–base systems has been developed by J. Bjerrum,[21] who points out that it is logical to inquire whether those bases which have the strongest affinity for hydrogen ions form the most stable complexes. A closely related series of ligands, such as ammonia and the primary aliphatic amines, must be studied if strictly comparable results are to be obtained, but the limited data available for such series make it necessary to consider also secondary, tertiary, and aromatic amines, heterocyclic nitrogen derivatives, aliphatic hydroxyamines, and so on. Bjerrum points out that the values of $\log K_{Ag^+}$ for complexes of such ligands with Ag^+ (and similarly for Hg^{++}) show a linear relationship when plotted against $\log K_{H^+}$ for the ligand. Exceptions to this rule occur in cases where stereochemical considerations show that the ligand molecules will, for one reason or another, not fit well around the metal ion.

Calvin and Wilson's measurements [22] on the stability constants of the complexes of diketones and hydroxy-aldehydes with cupric copper show a similar parallel between the strength of the ligand–Cu^{++} and ligand–H^+ bonds. Acetoacetic ester, acetylacetone and four derivatives of it, salicylaldehyde and a number of its derivatives were used. It is assumed that the enol forms of the substances co-ordinate so that the general reaction for k_1 can be written



the metal–ligand bonds being represented as dotted lines. If Cu^{++} is replaced by H^+ the equilibrium constant gives K_{H^+}. In all cases k_1 and k_2 were obtained for the copper complexes, and $k_1 > k_2$ as required by the statistical effect, but the values of k_1 and k_2 were not regarded as sufficiently well established to warrant any conclusions being drawn from the magnitude of $\log k_1 - \log k_2$. By taking an average value of $\log k_1$ and $\log k_2$ and making certain corrections, the authors obtain a value for $\log k_{av.}$ for each metal–ligand system, and on plotting $\log k_{av.}$ against $\log K_{H^+}$ they find that the ligands fall into at least two, and possibly four classes, each class giving a linear relationship. From this it is concluded that there

---

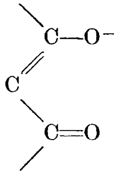
[20] Cf. ref. (2), p. 3.

[21] *Chem. Reviews*, 1950, **46**, 381.

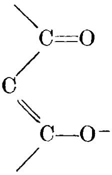
[22] *J. Amer. Chem. Soc.*, 1945, **67**, 2003.

are at least two factors influencing the strength of the metal–ligand bond, one of the same character for both copper and hydrogen, and the other quite different in the two cases. The first undoubtedly includes the effects of charge and charge distribution in the ligand, and the charge and size of the cation. The second is attributed to the double-bond character of the bonds between the three carbon atoms forming the chain between the two oxygen atoms.

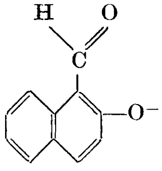
In terms of the resonance theory, the effective part of the ligand has two canonical forms, (*a*) and (*b*), and it is possible to express the state of the C–C bonds in numerical terms as a " bond order ".[23] The value of this will depend, in the case of the aromatic derivatives under consideration, on the rest of the molecule, and the effect of bond order on the relative values of $k_{\text{av.}}$ and K_{H^+} is well shown by the naphthoxide ions of 2-hydroxy-1-naphthaldehyde (VII) and of 2-hydroxy-3-naphthaldehyde (VIII).



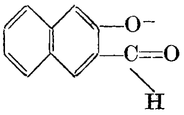
(*a*)



(*b*)



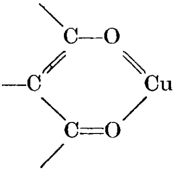
(VII.)



(VIII.)

The appropriate constants are : for (VII), log $k_{\text{av.}} = 7{\cdot}0$, log $K_{\text{H}^+} = 8{\cdot}4$; for (VIII), log $k_{\text{av.}} = 5{\cdot}8$, log $K_{\text{H}^+} = 9{\cdot}9$. The bond order of the two ring carbon atoms between the oxygen atoms is : in (VII), 1·66 ; in (VIII), 1·33. Thus the greater the double-bond character of this linkage the more stable the complex formed with copper. Exactly the same effect is seen with the other ligands studied, but the fact that (VII) and (VIII) are isomers lends this example particular significance since stereochemical factors and entropy-change differences are unlikely to be important.

Calvin and Wilson conclude that " the enolate resonance between (*a*) and (*b*) plays a part in the bonding of copper different to, and far greater than, it does in the bonding of hydrogen ". They suggest tentatively that the copper ion takes part in a conjugated 6-membered ring such as (*c*),



(*c*)

---

[23] Pauling, " Nature of the Chemical Bond ", Cornell Univ. Press, 1939.

the metal–oxygen linkages having some double-bond character. This may be compared with Chatt's suggestion[24] that the so-called "co-ordinate" bond between metals containing *d*-electrons and an atom containing a vacant *d*-orbital of sufficiently low energy always has a certain amount of double-bond character. This is due to the tendency of the metal to share these electrons with the atom which donates an electron pair to it to form what is normally regarded as the co-ordinate bond.

Effect of the Metal.—The discussion has, so far, been restricted to the effect of the ligand on the stabilities of complexes. Some information is now available which shows how the stabilities of the complexes of particular ligands vary with the position of the metal in the Periodic Table, this, of course, being a function of the electronic structure of the metal.

Mellor and Maley[25] studied the consecutive equilibrium constants of complexes of salicylaldehyde with a variety of 4-covalent bivalent metals, and by arranging the metals in order of decreasing stability of the complex, obtained the following series: $Pd > Cu > Ni > Pb > Co > Zn > Cd > Mg$. The values of $k_{av.}$ ranged from 7·39 for the palladium complex to 3·40 for the magnesium compound. In every case $k_1 > k_2$, and no abnormal effects were found. The same workers later[26] showed that a similar order is obtained by considering the complexes of pyridine and ethylenediamine.

The regularity occurring in this series, which is hidden by the haphazard choice of metals, was pointed out by Irving and Williams,[27] who showed, by choosing part of a transition series of metals (Mn^{++} to Cu^{++}) and plotting $\log k_n$ against the atomic number of the metal, that the stabilities of the complexes of a number of ligands increase with increasing atomic number to the end of the transition series, and then fall again (at Zn^{++}).

This is true only as long as bivalent states are considered and if $n \ngtr Z$. Since Z, by definition, is the number of ligand molecules bound with approximately uniform strength, when $n > Z$, as in the Cu^{++}–ethylenediamine system when $n = 3$, the stability is lower than would otherwise be expected for the metal.

Unless special factors, such as steric hindrance, which depends only on ionic size and the spatial arrangement of bonds, are operative, the order $Mn < Fe < Co < Ni < Cu > Zn$ is found for all ligands. The explanation of this regularity must be that the metal–ligand bond strength depends on the metal to a considerable extent, since it does not matter whether the atom attached to the metal is oxygen, nitrogen, or sulphur. It is not certain, however, that ligands containing arsenic, antimony, or phosphorus behave similarly.

The reason for the increase of bond strength with rise of atomic number is not yet clear, but the fall from copper to zinc is almost certainly due to the change from the situation occurring in cupric compounds, where *d*-orbitals are supposed to be available for bond formation, to that in zinc complexes where no *d*-orbitals of low energy are vacant.

[24] *J.*, 1949, 3340; private communication.

[25] *Nature*, 1947, **159**, 370.

[26] *Idem, ibid.*, 1948, **161**, 436.

[27] *Ibid.*, 1948, **162**, 746.

Calvin and Melchior [28] attempted to explain the phenomenon by comparing a number of properties of the ions under discussion, such as the ionic radius, heat of hydration, partial molal entropy, and ionisation potentials. The only obvious correlation was between stability and the second ionisation potentials of the elements, as had been previously pointed out by Irving and Williams.[25] These increase from 15·70 for Mn to 20·2 for Cu and fall to 17·89 for Zn. The authors point out that except for zinc this potential measures the energy required for removal of a *d*-electron, and they suggest that co-ordination replaces this electron, so that, in each case (except zinc), the hybridisation should involve *d*-orbitals.

It is well known that the complexes of salicylaldehyde with bivalent cobalt and nickel are paramagnetic and have 3 and 2 unpaired electrons respectively. This has been interpreted in the past as implying that the bonds are either ionic in character or involve tetrahedral sp^3 hybridisation. Calvin and Melchior suggest that the complexes are planar and involve bonds of a type intermediate between dsp^2 (planar, covalent) and ionic, and that in diamagnetic substances such as the complexes with salicylaldimine the increased basicity of the nitrogen atoms causes electrons to be pushed into the *d* shell of the metal, giving pure dsp^2 bonds.

This theory is interesting in that it provides an alternative explanation for the observed paramagnetism of a number of nickel and bivalent cobalt complexes. As a result of their extensive study of the magnetic properties of the complexes of these elements Mellor and Craig [29] suggested that the effective electronegativities of the atoms bound to the metal were very important factors in determining whether the complex would be diamagnetic or paramagnetic. There is also no direct evidence in support of the usual assumption that paramagnetic nickel complexes are tetrahedral. On the other hand, it would hardly be expected that a complex with bonds intermediate in character between ionic and covalent would show the magnetic moment expected for the pure ionic bond, and that there would be no gradual falling off in moment with increasing covalent character.

The observation which led to this theory, namely, that increased stability of complexes is paralleled by increase in the second ionisation potential of the metal, need not be interpreted in this way. The ionisation potential of a metal is only one factor influencing the stabilities of its complexes, and even if it is the controlling factor in the series of metals under consideration, it is not necessary to assume that, on formation of an ionic bond of the type existing in complexes, one of the electrons must occupy the *d*-orbital left vacant on ionisation of the metal. Hence there is no reason to postulate that the bonds existing in the complexes must involve hybridisation including this *d*-orbital.

It is possible, however, that the situation is analogous to that found when considering the relationship between stabilities of complexes and the basicity of the ligand. In this case, increasing basicity of related ligands causes increased stabilities of their complexes. If the basicity of the

[28] *J. Amer. Chem. Soc.*, 1948, **70**, 3270.

[29] *J. Proc. Roy. Soc. N. S. Wales*, 1940, **74**, 475, 495.

ligand is constant, then it would be expected that the stabilities of its complexes will depend on the electronegativities of the metal ions as measured by their tendencies to gain electrons. Copper has the highest ionisation potential of the metals under consideration and so has the greatest tendency to accept electrons, and, similarly, manganese has least.

It is emphasised that other factors may upset the order predicted in this way which, in any case, can only hold for a group of metals in one transition series. In particular, if the donating atom contains vacant *d*-orbitals of low energy, these may take part in the bond formation and overshadow the electronegativity effect.

Indirect Estimation of Stability

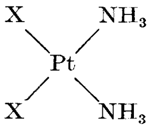
The work outlined above is based on measurements of equilibrium constants in aqueous solution, and the experimental conditions have to be such that the only complex species formed are MA to MA_N, the associated water molecules being ignored. It is therefore not possible to study complexes containing more than one type of ligand, and in particular, the effects of acid radicals on the properties of complexes cannot be investigated. Also, the complexes formed between many metals and ligands such as the substituted phosphines and arsines, higher aliphatic amines, and so on cannot be studied since they are often decomposed by water. In addition, those metals which form the most stable complexes, *e.g.*, the platinum-group metals and tervalent cobalt, cannot be investigated since the experimental methods require that equilibrium conditions should be fairly rapidly attained from either side of the reaction, and with these metals this condition is seldom fulfilled. J. Bjerrum [11] was able to study certain equilibria in the cobaltic ammine series by using carbon as a catalyst, but successive equilibrium constants for the ammines were not obtained. Information, of considerable interest in connection with the structures and stabilities of complexes where the limitations mentioned above apply, can be obtained in a variety of ways and some of the observations will be discussed below.

Anion Effect.—It is frequently found that for a given metal and ligand, the type of complex produced depends on the anions present in the solution. Thus β-furfuraldoxime gives different products when it co-ordinates with palladium, depending on whether palladous chloride, sulphate, or nitrate is used.[30] Such phenomena depend on a variety of factors, but it must be emphasised that the compositions of the solids obtained by such preparative methods do not necessarily indicate the natures of the complex species present in the solutions from which they were obtained. This is due, partially at least, to the fact that lattice forces may control the compositions of the solids which crystallise. It has been shown, however, that different acid radicals have very different abilities to co-ordinate with metals, and in some cases the compositions of the complexes in solution depend on the acid radical present.

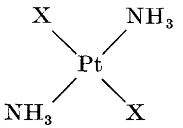
---

[30] Hayes and Chandlee, *Ind. Eng. Chem. Anal.*, 1942, **14**, 491.

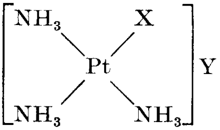
Such a conclusion was reached by King,[31] who studied conductometrically a number of *cis-* and *trans*-diammines and -triammines of bivalent platinum. These may be represented by the structures (XII), (XIII), and (XIV), where X and Y may be similar or different. He showed that whereas in some cases the anion X^- remains firmly bound to the platinum, giving non-electrolytes from the diammines and univalent complex ions from the triammines, yet in other cases the X^- groups may be replaced by water molecules, although usually the original substances are recovered on crystallisation. Platinum(II) complexes are divided by King into two groups on this basis, and the class into which any particular complex falls depends only on X^-. If the compound is unaffected by water, it may be concluded that X^- is bound firmly to the metal, but if X^- is readily replaced by water then obviously the metal–X bond is weaker than the metal–H_2O bond. It is found that NO_2^- (nitro), Cl^-, Br^-, I^-, and OH^- ions give complexes unaffected by water, whereas NO_3^-, SO_4^{--}, and picrate ions are readily replaced, giving aquo-complexes in solution.



(XII.)
cis-Diammine.



(XIII.)
trans-Diammine.



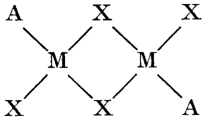
(XIV.)
Triammine.

That the importance of the metal–acid radical bond in determining the properties of certain complexes is not restricted to those of the platinum metals is shown by the properties of the complexes of copper with long-chain primary aliphatic amines.[32] This is an example of a Group I metal, many of the complexes of which can be studied in aqueous solution, exhibiting behaviour similar to that shown by the platinum metals, as long as the complexes are not subjected to the action of water. Complexes are formed of the type $CuX_2,2RNH_2$, where R is n-C_8H_{17} to n-$C_{18}H_{37}$ for example. They are soluble in non-hydroxylic solvents such as benzene, light petroleum, and chloroform, but are rapidly decomposed by water, alcohols, ketones, etc. Cupric chloride, bromide, acetate, etc., readily give bisamine complexes which are non-polar in character as is shown by their solubilities in hydrocarbon solvents and by other (unpublished) characteristics. The analogous sulphate complexes cannot be prepared directly and if made from the carbonates are very insoluble in non-polar solvents. Thus they are probably polar in character and are either salt-like or may have a " Zwitterion " type of structure. If X^- is NO_3^-, no complex can be prepared ; treatment of carbonate complexes with nitric acid causes total decomposition of the complex. From these facts it may be concluded that SO_4^{--} ions co-ordinate only with difficulty, and it is significant that King [33] found that hydration of sulphato-complexes proceeded more slowly than that of the nitrates and picrates.

---

[31] *J.*, 1938, 1338 ; 1948, 1912. [32] Burkin, *J.*, 1950, 122. [33] *Loc. cit.*

Other similarities between the platinum-group and other metals become evident on considering complexes which are soluble in organic solvents, showing that the essential processes of co-ordination are similar in each case. For instance, palladium forms a series of polynuclear complexes with substituted phosphines or arsines. These are stable, but the groups are somewhat labile as is usual in palladium complexes. Bivalent platinum gives similar, stable, derivatives,[35] and cadmium and mercury [34] also form fairly labile complexes with these ligands. The general formula for one class of these complexes is $[MX_2,A]_2$ and the structure is usually written as (XV) with the X atoms bridging the two metal atoms, X usually being Cl, Br, or NO_2 (nitro). Cuprous iodide gives a complex $[CuI,AsR_3]_4$ with a trialkylarsine,[36] four-fold polymerisation occurring to attain the usual Werner co-ordination number of 4 for the cuprous ion. Cuprous chloride, bromide, and iodide give with long-chain primary aliphatic amines similar derivatives $[CuI,RNH_2]_4$, but the bromide can also form $[CuBr,2RNH_2]_2$,[37] which decomposes in boiling benzene solution to give the tetrameric mono-amine complex and free amine. The importance of the " anion effect " is again shown in this case.



(XV.)

(XVI.)

Effect of Ligand.—The influence of the structure of the ligand is shown by the complexes of cuprous halides and *o*-phenylenebis(dimethylarsine) (XVI), which behaves as a chelating ligand.[38] Two series of compounds are produced, $[Cu(diarsine)_2]X$, and $[Cu(diarsine)_2][CuX_2]$, where X = halogen. The diarsine is such a powerful ligand that it controls the type of complex obtained.

The influence of the ligand is particularly noticeable in certain reactions of bivalent platinum, the complexes of which are invariably planar with the four atoms attached to the central platinum atom and arranged about it at the four corners of a square. On passing from a complex Pta_3b to either Pta_2b_2 or Pta_2bc by replacement of one *a* group by either *b* or *c*, the new substituent may take up its position in either the *cis*- or the *trans*- position with respect to *b*. Two examples are very well known :

$$K_2PtCl_4 + NH_3 \longrightarrow K[PtCl_3,NH_3] \xrightarrow{NH_3} cis\text{-}[PtCl_2,2NH_3]$$

$$[Pt,4NH_3]Cl_2 + HCl \longrightarrow [PtCl,3NH_3]Cl \xrightarrow{HCl} trans\text{-}[PtCl_2,2NH_3]$$

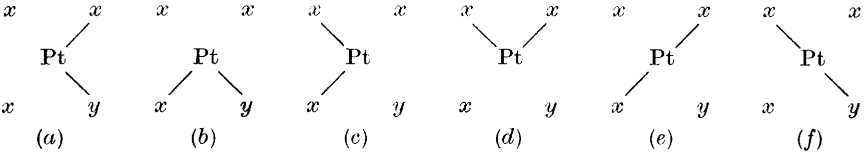
The interesting points are that only a single isomer is produced in each case, showing that the energies of activation of *cis*- and *trans*-replacement

---

[34] Mann, *Ann. Reports*, 1938, **35**, 151.
[35] Chatt, quoted by Nyholm, ref. (1).
[36] Mann, Wells, and Purdie, *J.*, 1936, 1503.
[37] Wilkins and Burkin, *J.*, 1950, 127.
[38] Kabesh and Nyholm, *J.*, 1951, **38**.

in each of the reactions must differ considerably, and that the isomer produced depends only on the ligands already present in the complex ion. In some cases a mixture of the isomers is obtained, but one is always produced in much larger quantity than the other. Chernyaev [39] interpreted the experimental results obtained by studying the orientation produced by a number of ligands, in terms of the " *trans*-influence " of the groups present in the complex. This may be defined as the effect of a ligand group on the strength of the bond between the ligand group in the *trans*-position to it, and the metal atom. A group with a high *trans*-influence loosens the *trans*-group and so makes substitution of it easier.

Syrkin [40] has attempted to explain *trans*-influence in terms of modern theory. It is assumed that in a compound Ptx_3y the four resonance structures (*a*)—(*d*) are important, " *ds* " hybridisation being postulated so that structures (*e*) and (*f*) need not be considered, the two " *ds* " bonds being at right angles. The four bonds are not equivalent and the group bound by the most ionic bond will be the one most easily replaced by substitution. If the Pt–y bond is more covalent than any Pt–x bond, then structures (*a*) and (*b*) will predominate and the x group *trans* to y will be bound by the least covalent bond and so will be replaced more easily than either of the other x groups. Thus, in general, the most covalently bound group in the molecule enhances the covalent character of the bonds to the groups in the *cis*-positions to it and makes the group in the *trans*-position more labile.



Among the factors influencing the character of the metal–ligand bond in a complex of a platinum metal is the electro-negativity of the atom bond. Consequently, the *trans*-influence decreases in the order I, Br, Cl, and is greater for S than for O and for P than for N. Also, partial double-bond character due to *d*-orbital overlap will increase the covalent nature of the bond, so that ligands with which this can occur will have high *trans*-influence. Similarly an unpaired electron such as occurs in the nitro-group forms a purely covalent bond, and this anion has a high *trans*-influence. The groups which cause greatest *trans*-labilisation, according to Syrkin, are $PAlk_3$, $SAlk_2$, $CS(NH_2)_2$, NO_2, unsaturated hydrocarbons (*e.g.*, ethylene), NO, and CO. Then follow, in order of decreasing effectiveness, $I > Br > Cl > NH_3 > H_2O$.

This theory is able to explain a great number of reactions and observations, and is a very useful systematisation, even if the resonance concept and *ds* hybridisation suggested are not accepted.

---

[39] *Ann. Inst. Platine*, 1927, No. 5, 118.

[40] *Bull. Acad. Sci. U.R.S.S., Classe sci. chim.*, 1948, 69.

An attempt has been made throughout this Review to present the underlying principles involved in the chemistry of complexes, and to substantiate theories by means of experimental data. As a result, the extreme paucity of information in this field may not be obvious, but it is, nevertheless, serious. The experimental method developed by Bjerrum [11] has stimulated work on certain metals and some ligands in aqueous solution, but an enormous field lies virtually unexplored because of the lack of suitable experimental methods. It is to be hoped that this situation will change in the near future.