374. *Complex-ion Formation. Part I. A General Discussion of Factors Influencing the Stability of Metal Ammines and Complex Ions.*

By W. S. FYFE.

Factors governing the co-ordination number, and the affinity of ligands for a single cation and of one ligand for a series of cations are discussed with particular reference to metal ammines. The formation constants of the complex silver ions formed by some substituted anilines are reported.

NUMEROUS papers and reviews have recently been concerned with conditions governing the stability of complex ions (*e.g.*, Bjerrum, *Chem. Reviews*, 1950, **46**, 381; Burkin, *Quart. Reviews*, 1951, **5**, 1). This paper considers, in particular, the application of electro-negativities and the neutrality principle (Pauling, *J.*, 1948, 1461) to the problem.

A study of the strength of a bond between a positive ion and a neutral dipolar molecule must cover several major problems. The linkage may be considered as purely electrostatic in origin, arising from the ion-dipole forces (cf. the term ion-dipole linkage). The number of ligands bound by an ion does not appear to obey a fixed rule or depend on the size of the central ion alone. Also, the conditions governing the affinity of a single cation for a series of amines, and of a single amine for a series of cations, are only partly understood. Resolution, even qualitative, of these uncertainties would be of much interest for the removal of ions and the stabilisation of oxidation states.

The Formation Process.—If it could be assumed that the attraction between an ion and a neutral dipolar molecule is purely electrostatic and that the molecules have rigid, unalterable dipoles, then we should expect that water, with a dipole moment much greater than that of ammonia, would not be replaced by the latter from a hydrated cation. This approach is obviously complicated by the different polarisabilities of molecules. For a series of amines, however, if orders of stability of the corresponding cations are calculated on the basis of dipole moments, little success is achieved.

The solvation of an ion may be considered as reducing the high field intensity about the ion. Pauling (*loc. cit.*) considers that when a ferric ion is placed in solution six water molecules become firmly bound to the central atom by partially covalent bonds. From the difference in electronegativities of the ferric ion and the oxygen atoms of the water molecules (Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, 1945, p. 70), it can be deduced that these bonds will be approximately 50% covalent. This means that the ferric ion gains three electrons, its effective charge being reduced nearly to zero. The positive charge must now be relayed to the hydrogen atoms of the water molecules, an additional charge of about $+ 1/4$ being thereby placed on each. The result is the formation of a large

complex ion with a low charge density. It must be remembered that, within the complex ion, iron will still be positive with regard to the oxygen atoms.

The same idea may be approached in a slightly different manner. The third ionisation potential of iron is in the vicinity of 30 ev. This is in excess of the energy necessary to remove an electron from the oxygen of the water molecule. It would be expected, therefore, that such an electron-transfer process should occur.

At the outside of the first shell of water molecules, covalent bonding with other water molecules to form a second shell of " chemically bonded " water must cease, for this would require bonding between hydrogen and oxygen. To form a true covalent bond, two orbitals (one from each atom) and two electrons are required. Oxygen has the electrons, but hydrogen has only one low-energy orbital and this is already filled. The possibility of hydrogen bonding is not thereby eliminated. This idea of absence of true chemical solvation between hydrogen and electronegative atoms or ions is confirmed by recent work by Johnson and Parton (personal communication) who found for hydrochloric acid a solvation number of unity. The one water molecule is considered to be attached to the proton, with no true solvation of the chloride ion. It also appears probable that, with the small additional charge on the peripheral hydrogen atoms of a solvated cation, water molecules which are hydrogen bonded in the second shell should suffer only a small reduction in degrees of freedom compared with molecules in the bulk of the solvent.

When an ammonia molecule approaches the hydrated metal ion, displacement of the water should occur because nitrogen, being less electronegative than oxygen, should form a more covalent bond with the metal. This in turn means that an ammonia molecule can more effectively distribute the charge on the cation. The increasingly covalent character of the bonds which are formed when electronegative atoms are replaced by less electro-negative atoms finds some support from magnetic data. In the paramagnetic complexes of ammonia and water with bivalent transition-metal ions, insufficient bond energy is available to supply the necessary energy to pair off the electrons in the d level and supply the six d^2sp^3 hybrid orbitals. The remaining s and three p orbitals must thus be used for bonding. In the more stable cyanides, where the carbon–metal bond is still more covalent and the low-energy d orbitals of the metal are used, pairing occurs. The resulting complexes are thus diamagnetic, or less paramagnetic than the parent ions.

Co-ordination Number.—The number of ligands bound by an ion appears to depend largely on two factors : first on the number of orbitals, hybridised or otherwise, that the metals have available for bond formation, and secondly on the number of linkages that will be required to reduce the charge on the central ion to a minimum. Size is not entirely a controlling factor, for the large silver ion takes two ligands and the mercuric ion four, while the smaller ions of the transition metals take six. Silver, which apparently uses a linear sp hybrid, could use an sp^3 hybrid and bind four ligands. By formation of two bonds with ammonia of approximately 50% covalent character, the charge on the silver ion is effectively reduced to zero, and further molecules will not be bound. It is of interest that the pyridine complexes of bivalent silver contain four pyridine molecules, not two as in all univalent silver complexes. The mercuric ion forms covalent bonds with ammonia of approxi-mately 80% covalent character, and after two ammonia molecules have been bound the charge will be considerably reduced. The third and the fourth ammonia molecule are known to be weakly bound.

With the bivalent transition-metal ammines, magnetic data (Selwood, " Magneto-chemistry," Interscience Publ., 1943) indicate that d orbitals are not extensively used in bonding. The s and the three p orbitals are thus available for bonding, and the number of ligands would be expected to be four. However, for these ions the bond with ammonia has less than 50% covalent character, and six ligands are required to reduce the charge to a minimum. Pauling (*J., loc. cit.*) considers that these six ligands are bound by the syn-chronised resonance of the sp^3 hybrid. However, as these bonds are fairly ionic, it appears possible that the ligands might be bound by the use of the three p orbitals alone, forming six half bonds (Rundle, *J. Amer. Chem. Soc.*, 1947, **69**, 1327). These compounds are certainly not to be considered electron-deficient but could perhaps be termed orbital-deficient. The use of p half-bonds of this type could account for the octahedral configuration of the

grouping. The greater covalent character of the bonds in cobaltic ammines, for example, which is due to the increased electronegative character of the tervalent ion, forces the electrons in the d level to pair and supply the d^2sp^3 hybrid. (It should be noted that the neutrality principle may only be accurate to about $\pm 1e$.)

The Ligand Effect.—In the following discussion the free energy of formation of the complex ion from the aquo-cation will be considered an index of the bond strength. As Burkin (*loc. cit.*) points out, this is only justified if the entropy of complex formation is small. However, in most of the cases to be compared and particularly in the ammonia complexes (data to be published later) the entropy changes per water molecule replaced are similar, so that free energy should be a reasonable index.

It has been shown (Fyfe, *Nature*, 1952, **169**, 69) that the stability of the silver complex ions formed with heterocyclic amines appears to be determined largely by the electron density assigned to the nitrogen atom of the amine. Measurements have now been made, with the same cell system, on some substituted anilines (see Table 1). The constants were measured in 59% (wt.) ethanol–water at 25° and express the equilibrium $Ag^+ + 2NH_2R = Ag(NH_2R)^+$, so that $K_f = [Ag(NH_2R)_2^+]/[Ag^+][NH_2R]^2$. Higher
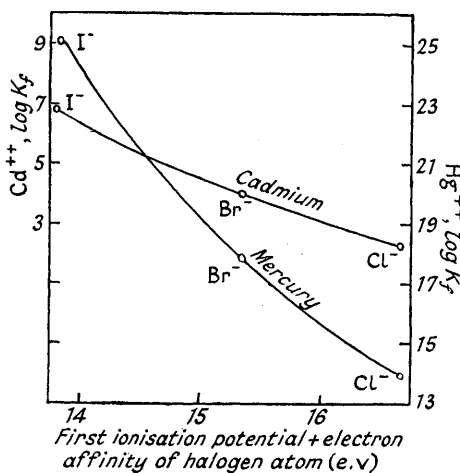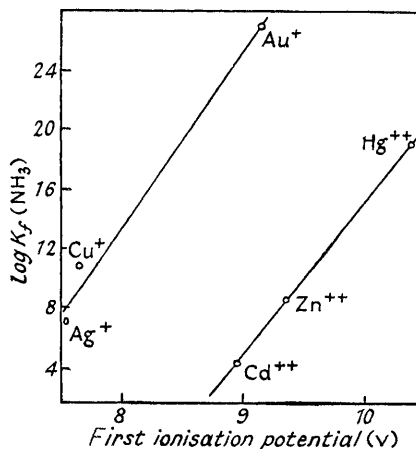
FIG. 1.
FIG. 2.

First ionisation potential + electron affinity of halogen atom (e.v)

First ionisation potential (v)

accuracy than that quoted was difficult to achieve, as many of the amines, in particular the nitro- and chloro-anilines, reacted fairly rapidly with silver ions, even when highly purified. The results demonstrate the expected effects of substituents. Groups which should increase the π-electron density of the nitrogen atom increase the stability and conversely.

TABLE 1.

Amine	log K_f ($\pm$ 0·05)	Amine	log K_f ($\pm$ 0·1)
Aniline	3·0	o-Chloroaniline	2·5
o-Toluidine	3·65	m-Chloroaniline	2·55
m-Toluidine	3·4	p-Chloroaniline	2·5
p-Toluidine	3·9	o-Nitroaniline	1·9
o-Bromoaniline	2·8	m-Nitroaniline	1·7
m-Bromoaniline	2·8	p-Nitroaniline	1·7
p-Bromoaniline	2·75		

In the aliphatic series (Bjerrum, *loc. cit.*) the same general considerations appear to hold. Thus the silver–di(amine) complexes increase in stability in the order methylamine <ethylamine < *iso*propylamine, which is in accord with the standard inductive order (see Table 2). It will be noted that, for aliphatic amines, the order of stability of the silver complexes is primary > secondary > tertiary. Two factors, both becoming more marked as the amine becomes more complex, appear to contribute to these orders : primarily a steric effect due to crowding of groupings around the central ion, and, secondly, the repulsion of the cation

by the polar groupings of the amine. The stability is also reduced by the addition of electron-attractive groups, as is shown by the ethylamines and hydroxyethylamines.

TABLE 2 (data largely from Bjerrum, *loc. cit.*).

Formation constants (log K_f) *of silver ammines.*

Ammonia	7·20	*iso*Propylamine	7·8 [a]	Triethylamine	4·8
Methylamine	6·68	*n*-Butylamine	7·48	2-Hydroxyethylamine	6·68
Ethylamine	7·30	Diethylamine	6·20	Tris-2-hydroxyethylamine	3·64

[a] Fyfe, unpublished work.

Complex Halides.—It was noted above that a connection appeared to exist between the stability of a complex ammine and the electron availability on the donating centre of the amine ligand. It is feasible that a similar correlation would hold in a series of complex halides, but there it should be possible to express the relation in terms of electronegativities, values for which are not available for the complex amine molecules. If we accept the hypothesis that the degree of electronegativity of the halide ion is a major factor in deter-
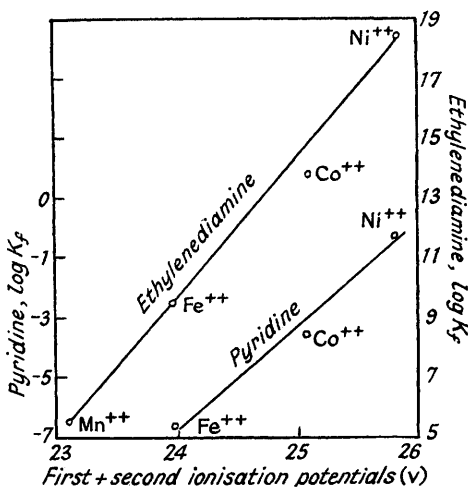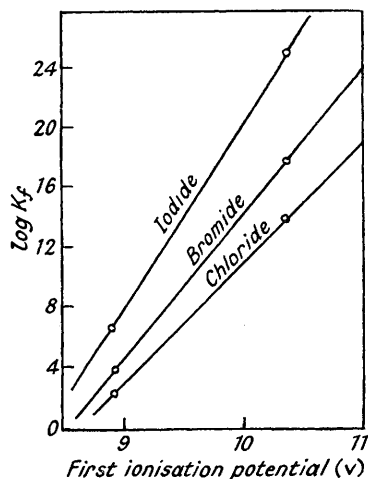
FIG. 3.

FIG. 4.

mining the degree of covalency in the bonds of the resulting complex ion, then this extent of covalency should be a function of the ionisation potential plus the electron affinity of the halogen atom. The suggested relation was tested on cadmium and mercuric halide complexes by plotting the logarithm of the formation constant against the sum of the first ionisation potential and the electron affinity of the halogen atom (Fig. 1). It is seen that the stability of the complex ion increases with increasing atomic weight of the halogen. This is also the order of decreasing electronegativity which should lead to increasing covalent character of the resulting bond. This, however, is by no means the only factor involved, as will be discussed later.

The Cation Effect.—The most complex problem in the study of metal ammines is that of explaining the order of stability of complexes formed by different cations with a given amine. Sufficient experimental work had been carried out to demonstrate that the order is generally independent of the nature of the ligand unless special factors such as entropy effects are operative. Such effects are most important for chelate compounds. The factors that would be expected to exert the greatest influence on bonding are : (*a*) the electronegativity of the metal; (*b*) the type of hybrid orbitals available for covalent-bond formation; and (*c*) the size of the cation. Factor (*a*), which is a function of the ionisation potential of the metal, should play a major role in determining the degree of covalent bonding; (*b*) will depend on the electronic structure of the metal atom; and (*c*) will

determine the ease with which the necessary number of ligands can be packed round the ion and will control steric factors and repulsion between ligands.

It is reasonable to compare stabilities only in isoelectronic series of metals where factor (*b*) can be kept constant. If this is done, it is found that the free energy of complex formation approximates closely to a linear function of the ionisation potential and thus, presumably, to the electronegativity of the metal atom. Similar conclusions were reached by Irving and Williams (*Nature*, 1948, **172**, 746) and Calvin and Melchior (*J. Amer. Chem. Soc.*, 1948, **70**, 3270). It must be emphasised that electronegativity values would be only approximate, since the electron affinity and the ionisation potential of a metal atom are seldom both known with accuracy. Plots of $\log K_f$ against either the first, or the first plus the second, ionisation potential of the metal are shown in Fig. 2 for the ammonia complexes of (*a*) zinc, cadmium, and mercury and (*b*) copper, silver, and gold. In Fig. 3 similar plots are shown for the ethylenediamine and pyridine complexes of manganese, iron, cobalt, and nickel. If a linear relation is assumed as suggested by the plots, then an equation of the type, $\log K_f = aI_p + C$, should hold. These plots have widely differing slopes and, from the discussion of the amine effect, it would be expected that for different amines the slopes would be a function of the electron availability on the ligand. In Fig. 4 values of $\log K_f$ for the halide complexes of the cadmium and the mercuric ion are plotted against the first ionisation potential of the metal. These slopes are at least in qualitative agreement with the theory. It will also be noted that the slopes obtained from the ammonia series for copper, silver, gold, zinc, cadmium, and mercury are similar, as might be expected.

TABLE 3. *Formation constants* ($\log K_f$) *of halide ion complexes of Group*-I B *and* -II B *metal ions* (*data from Bjerrum, loc. cit.*)

For the equilibrium $M^{z+} + nX^- \rightleftharpoons MX_n^-$ $\qquad K_f = [MX_n^-]/([M^{z+}][X^-]^n)$

Metal ion	Chloride	Bromide	Iodide	Metal ion	Chloride	Bromide	Iodide
Cu^+	5·6	6·0	9·0	Zn^{++}	−0·8	−2·4	−5·2
Ag^+	6·0	9·0	14·0	Cd^{++}	2·4	4·0	6·8
Au^+	17·2			Hg^{++}	14·0	17·8	25·0

In most of the cases mentioned, the size of the cation does not appear to play a very significant part, but several notable exceptions occur. As the ionisation potentials of zinc exceed those of cadmium, it might be predicted that zinc complexes should always be more stable than those of cadmium. However, although this is generally true, the order is reversed in the halide complexes (see Table 3). The same effect occurs with cuprous complexes. In these anionic complexes we are dealing with a complex ion in which there can be less charge distribution than in complexes formed by neutral molecules. With the zinc iodide complex ion, the radius ratio indicates that the maximum co-ordination number is four, while for cadmium, which still binds only four ligands, there is ample room for six. This indicates for zinc a very tightly packed system of anions around the central cation. Such a spatial effect should lead to a decrease in the stability of the complex, a result which will be enhanced by the mutual repulsion of similar ligands. With the larger cadmium and mercuric ions of the halide complexes the combined effect may well play a much smaller part in determining the stability. However, with smaller anions, such as cyanide and hydroxyl, and with neutral molecules, the reversal of order in the series does not occur. A similar effect may determine the reversal of the normal order in the complex halides of the cuprous and silver ions. With the small transition-metal ions, a similar steric effect may be responsible for the low stability of the halide ion complexes.

If we assume that a ligand can replace a water molecule on a cation only when it is capable of forming a more covalent bond and hence neutralising the charge on a cation more effectively than a water molecule does, then the fluoride ion, which is more electronegative than an oxygen atom, should not be capable of replacing the latter. It has been postulated (Baddeley, *J.*, 1950, 663) that fluorine can form π-bonds with greater facility than other halogens and that this facility decreases with increasing size of the halogen. As π-bonding increases the stability of some of the complex cyanides it might be possible for it to enhance the stability of complex fluorides. It must be remembered that electronegativity differ-

ences can be applied only to normal σ-bonding, and not to π-bonding, while the strength of a bond will depend on the balance of both types. However, preliminary calculations on Slater-type overlap integrals between metallic orbitals and fluoride or oxygen indicate that both σ- and π-bonding are less with fluoride than with oxygen. This it appears that the stability of fluorides must be attributed chiefly to the electrostatic interaction between a cation and the small fluoride ion. It may be noted that the most stable fluorides occur with either the most electronegative cations or with very small highly charged cations. (A more complete discussion on overlap integrals and this type of linkage will be submitted later.)

Note on Oxidation–Reduction Potentials.—From work on silver ammines, it is obvious that complex ions can be formed with widely differing stabilities. This is of particular importance, for it means that it is possible to vary the redox potential of an ion in a complex between wide limits. If the standard potential of a metal in water is known, and also the formation constant of the complex, then the redox potential of the complex ion can be calculated. Also, if a metal exists in two valency states, similar data enable the calculation to be made of the redox potential between the two complex ions from free-energy cycles.