Complex Formation.

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By N. V. SIDGWICK, C.B.E., D.Sc., LL.D., F.R.S.

THE principles involved in complex formation are now clear. Half a century ago Werner detected and emphasised its fundamental characteristic, the existence of a central atom having a definite number (independent of its periodic group) of other atoms or groups of atoms attached to it by non-ionic links; he systematised and extended our knowledge of such compounds, and established the principles of co-ordination chemistry on a firm experimental basis. When the electronic nature of valency was made evident, mainly through the work of Rutherford and Bohr on one side, and of G. N. Lewis and Kossel on the other, it was easy to apply it to the Werner system of compounds with the help of the co-ordinate or dative link (first suggested by Lewis in 1916), and to show the cause of the regularities which Werner had detected.

But while the principles are clear, and many of the more important groups of complexes have been recognised, a great deal still remains to do in systematising and completing the mass of experimental data accumulated by Werner and his successors. It is fairly obvious what in general are the factors which determine the stability of a complex molecule; but how their magnitudes are affected by the character of the atoms and groups concerned can only be discovered by a thorough review of the facts. It is this side of the subject which I propose to discuss. I have no startling new generalisations to put forward; nor on the other hand do I wish to trouble you with a mass of index learning, and as Pope says, to hold the eel of science by the tail; but perhaps some of the more important conclusions which emerge from such a study are worth consideration, if only as suggestions for future work.

A complex molecule is a group of covalently linked atoms, in which some at least of the shared pairs of electrons are not drawn one from each of the two atoms they link. This rather clumsy definition is the best we can give; the two shared electrons of the link may both be drawn from one of the two atoms (the typical co-ordinate link $A \leftarrow B$), or one of them may come from another non-linked atom, as in many complex ions. A much simpler but not completely satisfactory definition is that a complex molecule is one in which an atom has a covalency greater than its valency.

Complexes can thus arise by a variety of mechanisms, ranging from the simple direct co-ordination as in $(CH_3)_3B \leftarrow NH_3$ to such complicated electronic rearrangements as occur in beryllium "basic" acetate, $Be_4O(O{\cdot}CO{\cdot}CH_3)_6$, in whose formula no simple symbols can show the source of the shared electrons of each link, though enumeration proves that the necessary number is available. In the ordinary co-ordinate link the two atoms play different parts, and the one which contributes the two electrons is known as the donor, and the other as the acceptor. The more important factors in the stability of a complex AB_x are obviously the nature of the acceptor or central atom A—its atomic number, its valency, and its co-ordination or covalency number—and on the other hand the nature of the donor atom and of the other atoms (if any) attached to it, like the hydrogen atoms in ammonia or the oxygens in the nitro-group.

A very common and important form of complex is the complex ion—a complex molecule with a positive or a negative ionic charge; these can be formed by the co-ordination of donor atoms in such molecules as water or ammonia to the cation, as in $[Cu(\leftarrow NH_3)_4]SO_4$, or by the addition of anions to a neutral compound as in a ferrichloride $M[FeCl_4]$, where we may consider that a chlorine ion co-ordinates as donor to the iron in $FeCl_3$. The complex ion is characteristic of complex molecules in general, and may be regarded as typical of the whole class.

We may write the reaction by which a complex ion is produced

$$yM[B] + AB_x = M_y[AB_{x+y}]$$

giving for the equilibrium (the brackets here representing concentrations)

$$[AB_{x+y}]/[AB_x] \,.\, [B]^y = K$$

where K is the stability constant for the formation of the complex from its components, and is larger, the more stable the complex. Whether the complex salt can be made to separate from a solution of its components depends on the value of K, and the solubilities or solubility products of MB, AB , and $M_y[AB_{x+y}]$. Such salts are usually prepared from aqueous solution, but in any case from some liquid phase.

Usually M is an alkali metal, whose salt is likely to be very soluble, so that the separation of the complex salt will essentially depend on its having a large stability factor K and a small solubility, which will of course vary with M. The complex acids from which these salts are derived are nearly always strong (the central atom is normally unable to increase its covalency by taking up a hydrogen atom), and hence the alkaline salts are less soluble the heavier the alkali metal. This is why the potassium salts of complex acids are as a whole much better known than the sodium salts, while of some such acids only the cæsium salts have been prepared.

Another factor is the concentration of the binary compound AB_x. So far as this ionises, or is hydrolysed by the water, or dissociates into a lower AB compound and free B, this concentration is diminished, and the probability of the separation of the complex is less; the same thing happens if the solubility of AB_x is very small, as occurs with some fluorides. But all these unfavourable factors may be overcome if the stability of the complex is great enough (if K is sufficiently large).

After these general and *a priori* remarks, we have to consider the actual facts presented by preparational inorganic chemistry; this involves a survey of the whole field of complex chemistry, so as to discover what kinds of complexes are formed, and what are their stabilities. The results cannot as a rule be expressed quantitatively, and so they must to some extent depend on the taste and fancy of the surveyor; but I have tried to collect the facts and estimate their value as impartially as I can. Anyone else who carried out this survey would no doubt differ from me in some details, but not, I think, on any of the main conclusions.

The behaviour of elements in the formation of complexes depends on their atomic structure and their valency, and these are most easily expressed by the number N of electrons in the outermost group of the core when the atom has the valency in question. With elements of inert-gas structure (typical and A elements in their group valencies) N is of course 2 for the first period and 8 for the rest; with the B elements in their group valencies it is 18; with transitional elements in valencies lower than those of the groups it is greater than 8 and less than 18. A list of transitional values of N is given in Table I.

We may now consider the influence on the complexes of (1) the acceptor and (2) the donor.

TABLE I.

Values of N. (Sizes of Cores).

Valency.	Sc R.E.	Ti Zr Hf Th	V Nb Ta	Cr Mo W U	Mn — Re	Fe Ru Os	Co Rh Ir	Ni Pd Pt	Cu Ag Au
I					14	15	16	17	18
II	9	10	11	12	13	14	15	16	17
III	8	9	10	11	12	13	14	15	16
IV		8	9	10	11	12	13	14	
V			8	9	10	11	12	13	
VI				8	9	10	11		
VII					8	9	10		
VIII						8	9		

1. *Acceptors.*

Effect of Valency.—It is found that the tendency to form complexes is greatest with valencies of 2 and 3, though isolated examples of strong complex formation with other valencies can be found, as with monovalent silver and tetravalent platinum. This result is to be expected; on the one hand an increase of valency increases the tendency to covalency formation, while on the other a high valency involves a still higher covalency in the complex, so that it restricts both the number and (since the highest covalencies are less stable) the stability of the complexes formed. Thus trivalent iron can form complexes with covalencies of 4, 5, and 6; pentavalent phosphorus only with 6; hexavalent molybdenum can only form complexes with the rare covalencies of 7 and 8.

Effect of Atomic Structure.—In general this is what we should expect. Apart from the very strong tendency of beryllium and boron ($N = 2$) to complete their octets by co-ordination, which is a natural result of their small size, we find that the A ions of inert-gas structure ($N = 8$) have less co-ordination tendency than those of the B elements where $N = 18$ (pseudo-inert-gas structure): where the "inert pair" appears ($N = 20$, as in $\mathrm{Tl^{\bullet}}$ and $\mathrm{Sn^{\bullet\bullet}}$), the tendency is very small.

In the large class of transitional elements in the wider sense, with valencies less than those of their groups (*i.e.*, where $8 < N < 18$) the evidence shows that the tendency is small when N does not greatly exceed 8; from $N = 13$ to $N = 17$ it is larger than with any other N values (about a third of the known types of complex compounds are formed by central atoms from Group VIII); but nearly all the atoms of really high co-ordinating power are among those where $N = 14$ ($\mathrm{Fe^{ii}}$, $\mathrm{Ru^{ii}}$, $\mathrm{Os^{ii}}$, $\mathrm{Co^{iii}}$, $\mathrm{Rh^{iii}}$, $\mathrm{Ir^{iii}}$, $\mathrm{Pd^{iv}}$, $\mathrm{Pt^{iv}}$) and $N = 16$ ($\mathrm{Ni^{ii}}$, $\mathrm{Pd^{ii}}$, $\mathrm{Pt^{ii}}$, $\mathrm{Au^{iii}}$). Trivalent chromium ($N = 11$) is practically the only complex builder of the first rank outside these two classes.

It is of course obvious that since the atoms of elements in the later periodic groups have the smaller radii * they are the most likely to form covalencies, but we do not know why these two particular classes ($N = 14$ and 16) should be especially active. The anomalous position of chromium has long been recognised; trivalent chromium resembles trivalent cobalt not only in the number and composition but in the behaviour and even in the colour of its complexes, though the difference of 3 in the atomic number would seem to exclude the possibility of any analogy in structure.

Co-ordination Number.—This, which is the next point to consider, depends on the nature of A and B. As we should expect, it is in general greater, the higher the valency of A; thus for divalent platinum it is 4 and for tetravalent 6; for monovalent copper, silver, and gold it seldom exceeds 3, while for these elements in the polyvalent state it is 4 and sometimes 6.

Some central atoms favour particular co-ordination numbers in all their complexes; the most striking of these is auric gold, whose compounds are all complex, with a co-ordination number of 4. Others which are almost or quite confined to one co-ordination number are (the N values are added in parentheses): for a co-ordination number of 4, $\mathrm{Rh^{iii}}$ (12), $\mathrm{Pd^{ii}}$ and Pt (16): for the commoner number of 6, $\mathrm{Cr^{iii}}$ and $\mathrm{Re^{iv}}$ (11); $\mathrm{Ru^{iv}}$ and $\mathrm{Os^{iv}}$ (12); and finally $\mathrm{Co^{iii}}$, $\mathrm{Ir^{iii}}$, $\mathrm{Pd^{iv}}$, and $\mathrm{Pt^{iv}}$ (14): all these except $\mathrm{Cr^{iii}}$ and $\mathrm{Re^{iv}}$ have even values of N.

The co-ordinating power of a central atom can be greatly modified by the other atoms already attached to it. For example, many simple halides are strong acceptors, but the replacement of their halogen atoms by other groups markedly reduces this property. Thus boron trihalides will co-ordinate readily with nitrogen or oxygen atoms; boron trialkyl does so with nitrogen but not with oxygen, and boron trioxide will not attach itself even to nitrogen. In the same way the conspicuous power that stannic chloride has of taking up two molecules of aldehyde or ketone is greatly reduced if one of the four chlorine atoms is replaced by an alkyl group, and if more than one is so replaced it is destroyed. This effect of the replacement of halogens by alkyls is surprising, since there is presumably some back-co-ordination with the halogen but none with the alkyl, so that one would have expected the opposite effect.

The relation of the co-ordination number to the nature of B is also peculiar. It must ultimately depend on both A and B; but just as some A's have only one co-ordination number whatever the B, so some B's are much more limited than others in the variety

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* The differences are not large; the ions must be compared in the same valencies, so that the data are limited, but the following radii of divalent ions in the first long period are known: Ca 1·06, Mn 0·91, Fe 0·83, Co 0·82, Ni 0·76, Cu *ca.* 1·0, Zn 0·83.

of co-ordination numbers they show with any given central atom. For example the complex cyanides $\mathrm{M}_n[\mathrm{A(CN)}_x]$ and the nitro-compounds * $\mathrm{M}_n[\mathrm{A(NO_2)}_x]$ of any given central atom are usually found to be only of one type (not always both of the same type), while in other complexes, such as the ammines and the complex halides, each central atom forms several types of complex. Examples where the cyanide and nitro-complexes are only (or almost only) of one type are given in Table II.

TABLE II.

Co-ordination Numbers of Cyanide and Nitro-complexes.

	$\mathrm{Ag^{i}}$	$\mathrm{Cu^{ii}}$	$\mathrm{Hg^{ii}}$	$\mathrm{R.E.^{iii}}$	$\mathrm{Bi^{iii}}$	$\mathrm{Mo^{iii}}$	$\mathrm{Mo^{iv}}$	$\mathrm{Mo^{v}}$
CN	2	4	3(4)	—	—	8	8	8
$\mathrm{NO_2}$	2	5, 6	3	5	6	—	—	—

	$\mathrm{W^{iv}}$	$\mathrm{W^{v}}$	$\mathrm{Mn^{ii}}$	$\mathrm{Mn^{iii}}$	$\mathrm{Fe^{ii}}$	$\mathrm{Fe^{iii}}$	$\mathrm{Co^{ii}}$	$\mathrm{Co^{iii}}$	$\mathrm{Ni^{ii}}$
CN	8	8	6	6	6	6	6	6	4
$\mathrm{NO_2}$	—	—	—	—	6	—	6	6	6

	$\mathrm{Ru^{iii}}$	$\mathrm{Os^{iii}}$	$\mathrm{Os^{vi}}$	$\mathrm{Rh^{iii}}$	$\mathrm{Ir^{iii}}$	$\mathrm{Pd^{ii}}$	$\mathrm{Pt^{ii}}$	$\mathrm{Pt^{iv}}$
CN	—	—	6	6	6	4	4	6
$\mathrm{NO_2}$	5	5	6	6	6	4	4	6

The N values of these atoms are widely and more or less equally spread; the co-ordination numbers are nearly always the same for the cyanides as for the nitro-compounds, and most commonly 6. On the other hand with such complexes as the ammines or halides the number of types with one central atom is often large. It is possible that these numerous types are not really all different complexes, but that some are crystal aggregates. This is less likely to happen—the composition of the solid is less likely to differ from that of the complex—when the anions of which it is made up are those of weak acids like hydrocyanic or nitrous acid than when they are the anions of strong acids like the halogen hydrides, or neutral molecules like ammonia. Another possible reason for the difference, which applies to the halides but not to the ammines, is that while groups of a marked and fairly rigid shape, like the linear $-\mathrm{C{\equiv}N}$ and the Y-shaped $-\mathrm{N}\begin{smallmatrix}\nearrow\mathrm{O}\\ \diagdown\!\!\!\diagdown\mathrm{O}\end{smallmatrix}$, will only adapt themselves geometrically to particular types of complex, monatomic ions such as those of the halogens are more easily fitted in to a variety of structures.

A very remarkable cyanide group is that of the octacyanides $\mathrm{M}_n[\mathrm{A(CN)_8}]$; these compounds are formed by pentavalent and tetravalent molybdenum and tungsten ($N = 9$ and 10) but apparently by no other elements, though trivalent molybdenum ($N = 11$) gives the very similar 8-covalent complex $\mathrm{M_4[Mo(CN)_7(OH_2)]}$; the tetravalent molybdenum complex $\mathrm{K_4[Mo(CN)_8]}$ is the only 8-covalent structure which has yet been investigated by X-ray analysis (Hoard and Nordsieck, *J. Amer. Chem. Soc.*, 1939, **61**, 2853). It is to be noticed that potassium permanganate, which oxidises every other known compound of pentavalent molybdenum or tungsten to the hexavalent state, has no action on the octacyanides, showing both the extreme stability of these complexes and also that, though they occur with tetra- and penta-valent molybdenum and tungsten ($N = 9$ and 10), they cannot be formed by hexavalent ($N = 8$, in the group valency).

The few 5-covalent molecules whose structures have been established by physical means include only one complex, iron pentacarbonyl, and no complex ions. It is therefore possible that double salts which appear to have ions of this co-ordination number may be aggregates of simpler ions. They are fairly frequent among complex halides; otherwise, apart from a few ammines of undetermined constitution, they are practically confined to some of the nitro-compounds (of $\mathrm{Cu^{ii}}$, rare-earth metals, $\mathrm{Ru^{iii}}$, and $\mathrm{Os^{iii}}$); the relatively frequent occurrence of this type in the small group of nitro-complexes suggests that these have a true 5-covalent structure.

* The complex nitrites are of two isomeric types, with the $\mathrm{NO_2}$ group attached to the central atom by oxygen and by nitrogen respectively; the former ($\mathrm{A{-}O{-}N{=}O}$) are nitrito-compounds, and the latter $\left(\mathrm{A{-}N}\begin{smallmatrix}\diagup\!\!\!\diagup\mathrm{O}\\ \searrow\mathrm{O}\end{smallmatrix}\right)$, which are much more numerous and more stable, are properly called nitro-compounds.

The question whether the co-ordinating power increases or diminishes as the acceptor changes from a lighter to a heavier element in the same sub-group is not easy to answer. If we are considering the power of each element as a whole—in all its valencies—we must remember that in the B sub-groups a rise of atomic number leads to an increase in the stability of the lower valency due to the " inert pair ", a valency which is relatively unimportant in complex formation; thus in lead the tetravalent state has in itself more tendency to co-ordinate than the (" inert pair ") divalent, but its complexes are made less stable by their easy reduction to the lower state. On the other hand, in the transition elements of the A sub-groups and Group VIII a rise in atomic number diminishes the stability of the lower valencies; also with these elements the ionisation, which opposes complex formation, falls off rapidly with a rise of atomic number, even in one particular valency.

If we consider the change not in the sub-group as a whole, but in any specified valency of it, the conclusion seems to be that with the A elements in their group valencies ($N = 8$) the co-ordination tendency rises somewhat; with the B elements ($N = 18$) it is little affected; and in the transitional elements below their group valencies ($8 < N < 18$), and especially in trivalent and tetravalent palladium and platinum, there is a definite rise as we pass to the lower periods.

2. *Influence of the Character of the Donor.*

We have now to consider the donor side of the co-ordination. I have represented the donor by B in $A \leftarrow B$, but the group is more accurately written $A \leftarrow BC$, where B is the atom directly attached to A, on which the strength of the link mainly depends, and C stands for any other atoms that may be linked to it, which must to some extent modify the strength of the link. The heat of formation of the A–B link can seldom be determined in complexes other than the complex halides, and may be discussed when we come to them. As a rule we can only discover the affinity of particular B's for particular A's in a qualitative way from the consideration of the number and stability of the complexes they form.

Before we come to consider donor atoms in detail there is a preliminary point to be mentioned. Chelate groups, those which are linked through two atoms to the central atom and so form a ring, give complexes of exceptional stability. Thus, as Werner showed, ethylenediamine has a much greater power of co-ordination than ammonia, although it is a primary amine, and primary amines in general are much weaker donors than ammonia. Again, while phenol is a very weak donor—weaker probably than alcohol—catechol (*o*-dihydroxybenzene) is a very strong one, and has been shown to be capable of forming complex anions with 27 different metals. Oxalic acid forms far more numerous and stabler complexes than the monocarboxylic acids such as acetic. The list might be continued indefinitely. So general a tendency must be capable of explanation. Now with one important class of chelate compounds, the derivatives of β-diketones, β-keto-esters, salicylic acid and the like, there is a special reason for the stability, since the formation of the ring-complex introduces new possibilities of resonance. But with such groups as ethylenediamine, catechol, and the oxalato-group, no new resonance possibilities are brought in, and some other explanation must be sought.

The most probable is the very simple one that if one of the two co-ordinate links of a chelate group to the central atom is broken, the other will still keep it in place so that the broken link can be re-formed, whereas an atom or group which is attached only through a single link will drift away if that link is broken.

Another general question is the influence of other atoms attached to the donor atom B; but this is better considered under the individual donor elements. The most important of these are nitrogen, oxygen, and the halogens, and next to these carbon and sulphur. We may take them in the order of their periodic groups.

Carbon.—These include complexes formed with alkyls (such as $Na[Zn(CH_3)_3]$ and $M[Al(CH_3)_4]$): with unsaturated and aromatic hydrocarbons: with *iso*cyanides: with carbon monoxide: and perhaps we should add the complex cyanides. The number of elements which form complexes with carbon is limited, and the structures of the products are sometimes obscure. This is particularly true of the addition compounds with ethylenic and aromatic hydrocarbons. Cuprous and argentous solutions absorb ethylene : palladous and platinous addition compounds with ethylene and its homologues can be isolated. In these compounds it is clear that the $\mathrm{C{=}C}$ group acts as a donor and can replace a CO; indeed the ethylene compounds and the carbonyls show great resemblances, though the carbonyls are much more stable and more numerous.

The compounds with aromatic hydrocarbons are even more obscure; many of them are known only in the solid state, and may be crystal aggregates. We have, however, definite evidence from the electrical dipole moments that iodine and aluminium bromide can form co-ordinate links with benzene, and it is obvious that the aluminium at least must act as an acceptor.

The carbonyls are a very peculiar group. There is no doubt that the (chief *) structure is the linear form $\mathrm{A}\leftarrow\mathrm{C}\overset{\leftarrow}{\underline{=}}\mathrm{O}$, which may also be written $\overset{-}{\mathrm{A}}\mathrm{—C}\equiv\overset{+}{\mathrm{O}}$ or $\mathrm{A}{:}\mathrm{C}\vdots\mathrm{O}{:}$, all of which mean the same thing; with several carbonyls, especially nickel carbonyl $\mathrm{Ni(CO)_4}$, *X*-ray and electron diffraction have shown that it is the carbon that is attached to the central atom. A further and unexplained peculiarity is that in nearly all the carbonyl compounds, including those in which the CO is only one of several groups in a complex, the effective atomic number (E.A.N.) of the central atom adds up to that of an inert gas [as in $\mathrm{Cr(CO)_6}$, $\mathrm{Fe(CO)_5}$, $\mathrm{Ni(CO)_4}$]. The elements which take up carbon monoxide are mostly in, and all at least near, Group VIII : they are practically all included in the list :

Group VI A	VII A	VIII			I B	II B
Cr		Fe	Co	Ni	Cu˙	
Mo		Ru	Rh	Pd	Ag ?	
W	Re	Os	Ir	Pt	Au˙	Hg ?

The complex cyanides are a large and important group of complexes formed by some **30** central atoms (an element in **2** valencies being counted as **2**) ; many of these compounds are of quite exceptional stability. Their structures offer two obvious possibilities, $\mathrm{A—C}\equiv\mathrm{N}$ and $\mathrm{A—N}\overset{\rightarrow}{\underline{=}}\mathrm{C}$. It is curious that the structure has been but little discussed and is still uncertain. The cyanide ion $:\mathrm{C}\vdots\mathrm{N}:$ can evidently co-ordinate at either end; both nitriles and *iso*nitriles form complexes, and in silver cyanide AgCN the group is linked at both ends at once, for it has been shown (West, *Z. Krist.*, 1935, **90**, 555) that the crystal is made up of endless rectilinear chains $\mathrm{—Ag—C}\equiv\mathrm{N—Ag—C}\equiv\mathrm{N—Ag—}$; so too in the Prussian-blue compounds the CN group is attached at both ends (Keggin and Miles, *Nature*, 1936, **137**, 577). The evidence for the positions in the complex cyanides is not clear. The problem is made more difficult by the fact that the carbon and the nitrogen atoms are so near in atomic number that only the most accurate *X*-ray measurements can distinguish between them. In a few cases where such measurements have been made the results indicate that the central atom is attached to carbon. This was proved for the argenticyanides $\mathrm{M[Ag(CN)_2]}$ (Hoard, *Z. Krist.*, 1933, **84**, 231) and the octacyanide of tetravalent molybdenum (Hoard and Nordsieck, *loc. cit.*). Recent unpublished work by H. M. Powell has shown that the same is true in the ferrocyanides. This structure for the ferrocyanides is supported by other evidence. The products of their methylation, which have the compositions $\mathrm{[(CH_3)_6Fe(CN)_6]X_2}$ and $\mathrm{(CH_3)_4Fe(CN)_6}$, all on heating split off the alkyl *iso*cyanide and not the cyanide, so they must contain the grouping $\mathrm{CH_3{-}N{-}C{-}Fe}$, and the ferrocyanide itself presumably $\mathrm{N{-}C{-}Fe}$. Again, divalent platinum forms complex cyanides $\mathrm{M_2[Pt(CN)_4]}$ as well as addition compounds with both nitriles and *iso*nitriles, and the cyanides resemble the *iso*nitrile complexes in stability much more than they do the nitrile complexes.

So far all the evidence seems to be in favour of the A–C–N structure. But if we compare the tendency of various acceptors to form complex cyanides with their power of co-

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* This qualification is necessary in view of the undoubted occurrence of resonance in the carbonyls; the formula selected shows the spatial positions of the atoms, and seems the best expression of the behaviour.

ordination in other complexes to carbon and to nitrogen respectively, the results point rather in the opposite direction. Carbon is certainly the donor in the addition compounds formed by unsaturated hydrocarbons (the carbonyls have such special peculiarities that they do not help us here), and these, as we have seen, are formed by a limited number of acceptor elements almost all from Groups VIII and IB. These elements do indeed form complex cyanides, but so do many others such as vanadium, molybdenum, tungsten, rhenium, and in Group VIII iron, cobalt, and nickel, none of which are known to co-ordinate with hydrocarbons.

On the other hand, if we compare the complex cyanides with the ammines, we find that nearly all the strong cyanide builders (Cu^{i}, Ag^{i}, Au^{i}, Cu^{ii}, Fe^{ii}, Co^{iii}, Ni^{ii}, Ir^{iii}, Pd^{ii}, Pt^{ii}, Pt^{iv}) are atoms which also have a strong tendency to form ammines, in spite of the fact that the ammines are cationic and the cyanides anionic; though even here there are marked exceptions: for instance, tetra- and penta-valent molybdenum and tungsten, which form some of the stablest known cyanides, form no ammines, and trivalent chromium, giving as full and stable a series of ammines as any other element, forms no complex cyanides whatever. Again, as we have seen, there is considerable similarity between the cyanides and the nitro-complexes, which must have the nitrogen acting as donor, since the isomeric unstable nitrito-complexes (with A—O—N═O) are also known.

It is of course possible that some of the complex cyanides are linked through carbon and others through nitrogen, but if that is so it is curious that their properties do not show corresponding differences. On the whole it seems most probable that the cyanides have the carbon attached to the central atom, as the crystalline data and, so far as it extends, the direct chemical evidence indicate, and that the comparison of the cyanides with the carbon and nitrogen co-ordination compounds is misleading, because the presence of the triple link so greatly modifies the properties and affinities of the donor atom.

Nitrogen.—The most important class of nitrogen complexes is that of the ammines. This is so large that I can only discuss a few of the points which it raises.

Almost any halide other than an alkaline salt or a methane derivative will absorb ammonia at a low temperature, and the dissociation tension of the solid produced is often constant over a range of compositions. This does not prove that the composition at the end of the range is that of an ammine. The ammonia may react to give an ammonium salt, and until this has been detected and removed the composition of the mass is meaningless. Further, unless the tension is markedly less than that of ammonia at the same temperature, the solid may be a crystal aggregate with ammonia as one component. These facts do not invalidate the evidence from the formation of solids with ammonia, but they show that it must be examined with care, as indeed it often though not always has been.

The elements which have the greatest tendency to form ammines (Cu^{ii}, Be, B, V^{iii}, Cr^{iii}, Fe^{ii}, Co^{iii}, Ni^{ii}, Ru^{ii}, Ru^{iii}, Rh^{iii}, Ir^{iii}, Pd^{ii}, Pd^{iv}, Pt^{ii}, Pt^{iv}) are almost confined to Group VIII and the cupric and chromic compounds; as usual, the N values of 14 (Fe^{ii}, Co^{iii}, Ru^{ii}, Rh^{iii}, Ir^{iii}, Pt^{iv}) and 16 (Ni^{ii}, Pd^{ii}, Pt^{ii}) are prominent. Two elements of a very different kind are included in the list, beryllium and boron. But their affinity for nitrogen is only part of their general tendency to complete their octets by co-ordination; their ammines are very stable, but so also are their hydrates. For example, the tetrammine $[Be(NH_3)_4]Cl_2$ has a dissociation tension of only 6 mm. at 156°, but it is at once decomposed by water. This may be contrasted with the highly selective action of the cupric ion: an N/200-solution of a cupric salt in 0·4N-ammonia has been shown (Immerwahr, *Z. anorg. Chem.*, 1900, **24**, 269) to have a concentration of cupric ions not greater than 10^{-14}; that is, though the solution contains 140 times as many water as ammonia molecules, only 1 in 5×10^{11} of the cupric ions is hydrated.

There is a remarkable point to be noticed here. Co-ordination of an ion often tends to stabilise a higher as compared with a lower valency. The cobaltic ion Co^{+++} is so unstable that it decomposes water with liberation of oxygen; but in presence of ammonia, with which it forms a complex, it is so stable that it is produced from the cobaltous state by the action of atmospheric air. In many other cases, too, an unstable ion can be stabilised by conversion into a complex; this happens with both the cuprous and the argentic ions.

The point to notice is that this protection or stabilisation is not conferred by water; the water can replace the ammonia, but we must suppose that (at least with these ions) the linkage is comparatively weak.

The tendency to form ammines is usually much diminished when the hydrogen of the ammonia is replaced by hydrocarbon radicals. Apart from the very stable chelate compounds (formed, for example, by ethylenediamine, phenanthroline, and dipyridyl) the stability nearly always falls off in the order $NH_3 > NH_2R > NHR_2 > NR_3$; but pyridine behaves more like a primary than (what it is) a tertiary amine. This order of stabilities is well marked with the ammines of Cu^{ii}, Co^{ii}, Co^{iii}, and Ni^{ii}, but it does not seem to be invariable; with the stannic complexes $SnCl_4,2NR_3$ the effect, though in the same direction, is very slight, and with the ferric ammines it is actually in the reverse direction.

Oxygen.—Divalent oxygen with two covalencies has two lone pairs of electrons, and is able to share one or both of them in co-ordinate links: The compounds in which both are shared, giving a covalency of 4, are rare; they include such complexes as the " basic " acetates of beryllium, zinc, and zirconyl [*e.g.*, $Be_4O(O{\cdot}CO{\cdot}CH_3)_6$], whose stability must be much increased by resonance; the tetrameric thallous alkoxides $(Tl–O–Alk)_4$ with their cubic structure; and certain giant molecules, such as beryllium oxide.

In the great majority of its co-ordination compounds oxygen shares only one of its lone pairs with an acceptor, thus acquiring a covalency of 3. Complexes of this kind include the hydrates, especially of the ions, addition compounds with alcohols, ethers, ketones, and chelate derivatives of β-diketones and β-keto-esters, as well as of catechol and substituted catechols.

As judged by the tendency to form co-ordination compounds the affinity * for oxygen is much higher than for nitrogen in the majority of elements with non-transitional cores ($N = 8$ or 18), but there are some exceptions, especially in Groups IB and IIB, the affinity being small in Cu^{i}, Ag^{i}, Au^{i} and in Cd, Hg, and in both subgroups falling off as the atomic weight rises.

The general position of water is easily stated. The great majority of atoms or groups which co-ordinate with it are cations, as is to be expected, since a positive charge makes an atom more ready to act as an acceptor. The hydration follows the normal rules of covalency formation, being more intense (and more extensive so far as the covalency limits permit) the greater the charge on the cation and the smaller its size. Hydration is slight with the heavier alkali metals, and with silver and mercury, the peculiar position of the last two elements being presumably due to their small affinity for oxygen. The hydration of anions is relatively rare, but not unknown; it occurs, for example, in the sulphate and oxalate ions. With anions the water must be attached through its hydrogen, by means of a " hydrogen bond "; the nature of this cannot be discussed here,† but it is certainly not co-ordination in the usual sense of the sharing of a second pair of electrons by the hydrogen, and it should not be represented in formulæ by an arrow.

When we pass from water to its organic derivatives, the strength of the co-ordination diminishes, the order being water > alcohols > ethers, as with ammonia and the amines. The comparison between ether and either alcohols or water is complicated by the occurrence of reactions with the hydroxylic compounds; for this reason the very stable compounds of ether with, for example, the Grignard reagents can have no parallel with water or alcohol. On the other hand molecules with doubly linked oxygen, aldehydes and ketones (including quinones) co-ordinate more strongly than ethers; thus acetaldehyde will expel ether from the molecule $(Et_2O)_2MgBr_2$. Tin is especially remarkable for the number and stability of the compounds of the type $SnCl_4,2O{=}CR_2$ that it forms.

There are a large number of chelate complexes formed by co-ordination through two oxygen atoms. Unlike the chelate nitrogen complexes, which are nearly always formed

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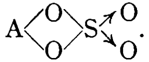
* Affinity in this sense is large for oxygen as well as for nitrogen with Be, Cr^{iii}, Fe^{ii}, and the platinum metals generally.

It is greater for oxygen than for nitrogen with the alkaline earths; Ga, In, Tl; Ti, Zr, Th, Si, Ge, Sn; V^{v}, V^{iv}, Nb^{v}, Ta^{v}; Mo^{v}, U^{vi}, U^{iv}; Fe^{iii}, Co^{ii}.

It is less for oxygen than for nitrogen with Cu^{i}, Ag^{i}, Au^{i}, Cu^{ii}; Cd, Hg; V^{iii}, Co^{iii}, Ni^{ii}.

† See Pauling, "The Nature of the Chemical Bond," 1939, Chap. IX.

by addition, and so are usually cationic, most of the oxygen rings are formed by the replacement of hydroxylic hydrogen, and are neutral or anionic; this is natural, since hydrogen is much more easily replaced in water than in ammonia. These complexes comprise firstly neutral derivatives of the mono-enolic forms of β-diketones and β-ketonic esters, such as acetylacetone, acetoacetic ester, and salicylic compounds, whose stability is increased by resonance; and secondly the anionic "ato" complexes formed from dibasic oxy-acids and *o*-dihydroxybenzenes, such as the sulphato-complexes containing the group  $\mathrm{A}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}\mathrm{S}\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{O}\end{smallmatrix}$. The last are formed by a variety of acids, sulphurous, sulphuric, thiosulphuric, phosphoric, etc., as well as the carboxylic acids carbonic, oxalic, malonic, and others. The known complexes are very numerous and often very stable; several of them have been resolved into optically active forms.

Sulphur.—Formally sulphur resembles oxygen, having in the dicovalent state two unshared pairs of electrons, but the tendency of sulphur to form complexes with other elements by no means follows that of oxygen. Thus the attachment of monovalent copper, silver, and gold, and of mercury, is much stronger to sulphur than to oxygen, while that of beryllium, divalent copper, trivalent gold, and other elements is much stronger to oxygen.

Of the double or complex sulphides many are of unknown structure, for example, $M[CuS_4]$ and $(NH_4)_2PtS_{15},2H_2O$: while others, such as M_3PS_4 and M_3AsS_4, are no doubt the sulphur analogues of familiar oxy-salts.

Of the complexes in which sulphur definitely acts as a donor, the most important are those formed by hydrogen sulphide, mercaptans, and thioethers, and the chelate rings formed through a sulphur and an oxygen (as in the complex thiosulphates) or through two sulphur atoms. The elements which can co-ordinate as acceptors with the sulphur in these various molecules are those given in Table III.

TABLE III.

Elements co-ordinating with Sulphur.

Be						
	Al					
		Ti		Ni	Cu^{i}	Zn
					Cu^{ii}	
		Sn	Sb	Pd^{ii}	Ag^{i}	Cd
				Pt^{ii}	Au^{i}	Hg
				Pt^{iv}	Au^{iii}	

Nearly all of these will be seen to come from the three sub-groups VIII3, IB, and IIB, the *N* values being 18 (7), 16 (4), and 8 (3). It should be noticed that these few elements include practically all those which co-ordinate with unsaturated hydrocarbons (Pd^{ii}, Pt^{ii}, Cu^{i}, Ag^{i}, Au^{i}, Hg).

The known complexes of hydrogen sulphide and the mercaptans are few; far more are formed by the thioethers: the tendency of sulphur to act as a donor seems to increase in the order $SH_2 < SHAlk < SAlk_2$, the exact opposite of what happens with nitrogen and oxygen. So few thioketone complexes are known that we cannot say whether they are more readily formed than those of the thioethers, as with oxygen.

Complex Halides.—The known types of complex halides are more numerous than those of any other kind of complex ions, and almost as many as all the rest put together. The fact that there are four halogens, and the absence of complications due to other atoms attached to the donors, make the relations in this group of complexes especially illuminating. Further, the heats of formation of the A–halogen links are known for many elements, and their influence on the complex formation can be studied.

Complex halides have been described with every number of halogen atoms in the molecule from 2 to 8.* But the evidence for the existence of the great majority of them is the analysis of the solid phase; only some of these 7 types—probably only the di-,

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* Here, as elsewhere, complexes with 2 or more central atoms in the molecule are not dealt with, as their constitutions are nearly always too uncertain.

tetra-, hexa-, and a few of the hepta-halides—have had their crystal structures determined in any examples, and it is only when this evidence has been obtained that we can be sure we are dealing with a single salt and not with a crystal aggregate. The fact that the alkaline halides are not hydrolysed in water, and the adaptability of the monatomic halide anions to various crystalline structures, make it exceptionally likely that such crystal aggregates will be formed. That this is not an imaginary danger has been shown in several instances. Thus *X*-ray analysis has proved that a salt of the composition $K_2CuCl_4,2H_2O$ is really a closely packed aggregate of (planar) molecules of $CuCl_2,2H_2O$, chloride ions, and potassium ions (Hendricks and Dickinson, *J. Amer. Chem. Soc.*, 1927, **49**, 2149 ; Chrobak, *Z. Krist.*, 1934, **88**, 35. See L. Pauling, *op. cit.*, p. 101) ; that the salt Cs_3CoCl_5 is an aggregate of Cs cations with $CoCl_4$ and Cl anions (Powell and Wells, J., 1935, 359), and that a salt which has the composition $CsAuCl_3$, and thus appears to contain divalent gold, should really be written $Cs_2Au^iAu^{iii}Cl_6$, and that the solid is made up of Cs cations and two kinds of anions, linear Au^iCl_2 and planar $Au^{iii}Cl_4$ (Elliott and Pauling, *J. Amer. Chem. Soc.*, 1938, **60**, 1846).

It is therefore evident that the structures of individual complex halides must be accepted with reserve except where they are supported by crystal analysis. But as a rule, when a double halide is assumed to be complex, there is good evidence (for example, from the solubilities) that it contains complex ions, though they may not correspond to the composition of the solid. We can therefore safely draw conclusions from the experimental data as to the relation of the stabilities to the nature of the components.

There is little to be said as to the effect of the central atom on the stability ; complex halides are formed by almost all elements that have any power of acting as acceptors. But the influence of the halogen is marked.

The stability is clearly dependent on the heat of formation of the A–halogen link in the complex. This cannot be measured for the complex salt, but its value in the simple halide $A(hal)_x$ from which the complex is derived, is often known.* Where they have been determined, the heats of formation are always in the order

$$A–F > A–Cl > A–Br > A–I.$$

If we exclude the F–F link, whose abnormal weakness can be explained on theoretical grounds, there is no known exception to this order. It is true that most of the A atoms for which the heats have been measured are electro-negative, but such metals as silver, beryllium, mercury, and tin are included, so that we may assume the rule to be general. In the observed cases (which include some 20 kinds of A atoms) the mean relative values are :

A–F	A–Cl	A–Br	A–I
1·47	1	0·84	0·69

For our purposes the important value is that of the link in the complex, where the covalency is always greater than in the simple halide. But there is evidence that the value does not change much with the number of links ; this is shown in the following examples :

P–Cl	Sb–Cl	I–Cl	Al–Cl
in PCl_3 62·8	in $SbCl_3$ 68·0	in ICl 51·0	in $AlCl_3$ 91·6
in PCl_5 53·4	in $SbCl_5$ 55·6	in ICl_5 42·0	in Al_2Cl_6 73·7
Ratio 1 to 0·85	0·82	0·82	0·80

As the change with increase of covalency is presumably in the same direction whatever the halogen, we may take it that in the complex halides also the heats of linkage to the same central atom retain the order A–F > A–Cl > A–Br > A–I.

Now whenever the relative stability of the different complex halides of a given central atom can be compared, it is found that the order for the last three halogens is invariably † Cl > Br > I, which agrees with the heat values. But the fluoride is sometimes more and

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* The heat values given here and later are the heats of formation of the link in the gaseous halide from its atoms. They are taken partly from Pauling's " The Nature of the Chemical Bond," p. 53, and partly from the data in Bichowsky and Rossini's " Thermochemistry," 1936.

† It is possible that the reverse order holds with the complex halides of mercury.

sometimes less stable than the chloride. Where it is more stable, this is again in agreement with the heats of linkage. Where it is less stable, some other cause must be operative. Possible causes are (1) that the simple fluoride does not exist, (2) that it is very sparingly soluble, (3) that it is highly hydrolysed by water. The data show that there are some 22 central atoms whose complex fluorides are more stable than the chlorides, and 34 where the fluoride is either unknown or less stable than the chloride. The following table shows the number in each division which come under the headings (1), (2), and (3) respectively; the " normal " are those to which none of these headings apply.

TABLE IV.

	Binary fluoride.	1. Non-exist.	2. Insol.	3. Hydrol.	Normal.
Stability of	F > Cl (22)	2	1	2	17
complex	F < Cl (34)	17	4	9	4

These results make it clear that the normal position is that the complex fluoride is the more stable, and that the factors (1), (2), and (3) discourage the formation of complexes but do not necessarily prevent it.

This concludes my summary of the conditions and results of complex formation; I hope it may be of use as indicating some of the lines along which a more detailed study of complexes is needed.