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REPORT NO. BRL/146

DEPARTMENT OF INORGANIC CHEMISTRY

A DISCUSSION ON CO-ORDINATION CHEMISTRY

held on 21st - 22nd September, 1950.

Prepared by

J. Chatt and
R.G. Wilkins

(Circulation list on back of front cover)

AKERS RESEARCH LABORATORIES

"The Frythe",
Welwyn,
Herts.

May, 1951.

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A DISCUSSION ON CO-ORDINATION CHEMISTRY

held at The Frythe on
21st - 22nd September, 1950

A symposium on co-ordination chemistry, at which there was an attendance of forty, was held at the Butterwick Research Laboratories of I.C.I. Ltd., at Welwyn on 21st - 22nd September, 1950. The Chairmen were Dr. J. Chatt (first day) and Dr. F.G. Mann, F.R.S. (second day). The first day's programme was concluded by a dinner and social evening which provided an opportunity for an informal exchange of views. The guests were welcomed by Mr. M.T. Sampson, and Professor N.V. Sidgwick, F.R.S. opened the symposium with an account of the history of the subject to about 1925.

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PREFACE

This report is the record of a unique occasion, when for the first time in many years, a symposium devoted entirely to co-ordination chemistry was held in Great Britain. It was attended by most of the leading British Chemists in this field and several distinguished guests from overseas.

We have attempted to make this report as complete as possible. It has been compiled from our stenographer's notes and from author's manuscripts. There has been no attempt at uniform treatment of the contributions which vary in style and completeness according to the author's notes. That so complete a report has been possible, is largely due to the kind co-operation of the speakers, to many of whom we had to submit our rough notes for amplification. We apologise for any errors and omissions which may nevertheless appear.

Finally, we should like to thank all who attended the symposium for their enthusiasm and co-operation, and also our many colleagues who helped with the organisation of the meeting and the preparation of this report. May we express a hope that we shall see a revival of interest in our subject and that this meeting will be a forerunner of others.

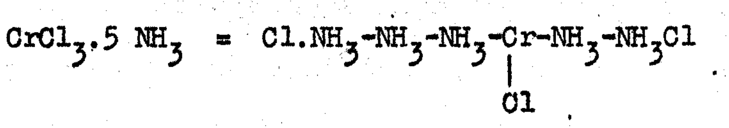
GENERAL INTRODUCTION
TO
CO-ORDINATION CHEMISTRY

By Prof. N.V. Sidgwick, F.R.S.

(Oxford University)

I thought I could best comply with the request with which you have honoured me that I should introduce this discussion of Co-ordination Chemistry, by giving a brief account of the earlier history of the subject, down say to 1925.

Early in the last century it became recognised that the salts of some polyvalent elements, especially chromium, cobalt and platinum, could combine with varying numbers of ammonia molecules to form substances with compositions such as $CrCl_3.6\ NH_3$; $CoCl_3.6\ NH_3$; $PtCl_2.2\ NH_3$ and $PtCl_4.2\ NH_3$; and whose compositions were very difficult to explain by formulae. Blomstrand supposed that the NH_3 molecules were attached to one another in open chains through pentavalent nitrogens, as in



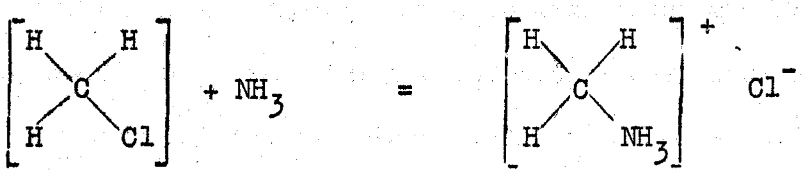
$$CrCl_3.5\ NH_3 = Cl.NH_3\text{-}NH_3\text{-}NH_3\text{-}\underset{\displaystyle Cl}{\underset{|}{Cr}}\text{-}NH_3\text{-}NH_3Cl$$

This was obviously improbable; it gave no explanation of the properties of the products and of their ionisation: and they never could be converted into compounds with even two nitrogen atoms joined together. The number of these substances rapidly increased, and it was found that other molecules, especially water, could replace the ammonias wholly or in part.

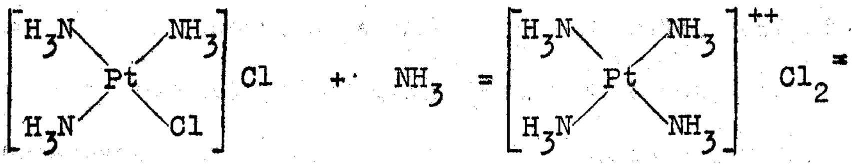
Then in 1893 Alfred Werner produced an extensive paper on these compounds. He assumed that the complex molecules were held together by a new force which he called co-ordination. This was capable of binding to one central atom irrespective of its valency a specified number, usually 4 or 6, of other atoms or groups which might be ionisable radicals like Cl or NO_2, or whole molecules like NH_3 or H_2O. He found that whenever an NH_3 molecule was removed, one of the acid radicals took its place, so that the number of groups in the complex remained the same; also that the radical that entered the complex was no longer ionisable, as in $[Cr(NH_3)_6]Cl_3$, $[Cr(NH_3)_5Cl]Cl_2$, and so on down to $M[Cr(NH_3)Cl_5]$. He concluded that the determining factor in these complexes was the number of groups of any kind attached to the central atom, and that any groups outside this were ionised. He invented the use of the square bracket to enclose the atoms of the complex, and any groups outside it were shown by experiment to be ionised.

This theory was little regarded by chemists in general until in 1911 Werner showed that some of these 6-co-ordinated compounds such as $[CoCl(NH_3)(en)_2]Cl_2$ should be optically active if we assume that the 6 groups of the complex are at the points of an octahedron, and succeeded in resolving them; this convinced chemists, and especially organic chemists, that the Werner compounds must be taken seriously.

It thus appeared that there are two different kinds of chemical structure, one (the ordinary organic theory) in which the number of links is determined by the valency of the atoms, and the Werner theory, applicable to inorganic compounds, in which the valency of the atoms is of no importance, compared with the number of groups attached to the central atom in the complex. It was still more curious that the co-ordination theory could be applied to organic compounds also, with a co-ordination number of 4, and sometimes in considerable detail, as in the equation:



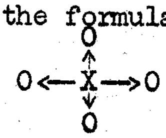
parallel to:



though in organic compounds it is less useful than the ordinary structural theory.

This made it clear that the true structural theory must comprise both of the other two. How this could be was shown first by G.N. Lewis in 1916 (J.A.C.S. 1916, <u>38</u>, 762). He here gave for the first time an explanation of the nature of non-ionised links (covalencies) as being due to the sharing (in some way) of two electrons between the two linked atoms. He pointed out that normally such a link merely involved replacing by two dots the single line representing a link; but that this idea made possible certain formulae of great significance not previously contemplated. It was obviously possible that the two linking electrons might come, not one from each atom, but both from one of them.

$$A. + .B = A:B \quad \text{or} \quad A: + B = \overset{+}{A}:\overset{-}{B} \quad \text{or} \quad A \longrightarrow B \quad .$$

In this way a divalent element like oxygen could form a saturated linkage with an atom which had a pair of unshared electrons. He pointed out that this made it possible to write the formulae of the ions ClO_4, SO_4, PO_4 and SiO_4 on the common type  $O \longleftarrow \underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{X}} \longrightarrow O$ where the number of electrons is unaltered by the linkage, and so these ions must have the electrovalencies 1, 2, 3 and 4 respectively.

This was the original statement of the nature of the dative or co-ordinate single link. It was soon realised that this explained the co-ordination compounds of Werner, and reconciled their structures with those of organic compounds in general. Consider the neutral compound $[Pt(NH_3)_2Cl_4]^0$. The two NH_3 groups are attached to the platinum atom by two pairs of shared electrons derived from the two nitrogens: and the 4Cl atoms each by a pair, one from the Cl, and one from the Pt. If a (neutral) Cl atom is removed, it will take one of these electrons with it, leaving the other behind. Then the 5 groups on the Pt must be increased to 6 to secure stability. If this is done by adding an NH_3, the Pt will gain two electrons of the co-ordinate link. As it had a stable number before, it now has one too many: it will, therefore, lose this, and acquire a positive charge. Thus we have $[Pt:Cl]^0 \longrightarrow [Pt.]^0 \longrightarrow [Pt:NH_3]^0 \longrightarrow [Pt:NH_3]^+ + e$ as in the action of ammonia on methyl chloride.

The bearing of Lewis' new type of link on the structure of these co-ordinated compounds of Werner has been mentioned first, because it was the most startling result of his discovery; but of course there were many others, and for the last 25 years at least, the co-ordinate link has been a recognised part of many structural formulae. It is often doubtful whether a link to, say, oxygen is a co-ordinate or an ordinary double link. For example we might write phosphorous oxychloride $\mathrm{Cl_3PO}$ either as $\begin{array}{l}\mathrm{Cl}\diagdown\\ \mathrm{Cl{-}P{\rightarrow}O}\\ \mathrm{Cl}\diagup\end{array}$ or as $\begin{array}{l}\mathrm{Cl}\diagdown\\ \mathrm{Cl{-}P{=}O}\\ \mathrm{Cl}\diagup\end{array}$. This question entered on a wholly new stage when, some 16 years ago, the theory of resonance was accepted. Except where the covalency rule forbids, as in $\mathrm{R_3N{=}O}$, or when there are stereochemical difficulties, these two kinds of link must be in resonance with one another. An important example of this is the $\mathrm{XO_4}$ ion, with which Lewis started: this might be $\begin{array}{c}\mathrm{O}\\ \uparrow\\ \mathrm{O}\leftarrow\mathrm{X}\rightarrow\mathrm{O}\\ \downarrow\\ \mathrm{O}\end{array}$ (covalency 4) or $\begin{array}{c}\mathrm{O}\\ \|\\ \mathrm{O}=\mathrm{X}=\mathrm{O}\\ \|\\ \mathrm{O}\end{array}$ (covalency 8) or anything between them, so far as the covalency limit of X allowed. No double links are allowed in the first short period but two are possible in the second short and first long periods. Except in the first case there must always be some resonance between the single and double links, and we have to try and discover the relative predominance of the two forms.

The problems of co-ordination compounds have in the last 25 years developed, and are still developing, along several lines, the more important of which are the concern of the papers that follow. There is the preparation of new co-ordination compounds (Dr. F.G. Mann, Dr. R.S. Nyholm), so as to extend our knowledge of the relation between the co-ordinate stability, and the co-ordination number and the nature and valency of the central atom and of the attached groups; this involves the quantitative determination of this stability by the measurement of the heats of linkage and of the equilibria in dissociation (Prof. Schwarzenbach, Dr. Irving).

A further point is a comparison between the properties of a co-ordinate link and those of a normal single covalency between the same atoms. It is very remarkable that so far as we know the links $\mathrm{A{-}B}$ and $\overset{+}{\mathrm{A}}{-}\overset{-}{\mathrm{B}}$ are almost identical in properties, especially in their length (so far as resonance does not interfere) and in their heats of formation.

Another line is the stereochemical (Prof. Jensen, Dr. R.G. Wilkins, Dr. A.F. Wells); an interesting point here is the light which these compounds may throw on the stereochemical arrangements of covalencies of 5 and above where some of the links are double. With the octet we know what these are from other evidence: but at present there seems to be no direct experimental evidence of this where the valency group is larger than 8, and the theoretical evidence seems to be rather slight. But it is clear that the resonance between a structure with A-B and one with A=B will depend on how far this change alters the positions of the atoms.

Behind these questions, most of which are purely experimental, lie the deeper theoretical problems of the nature of the orbits which take part in the structure (Mr. L.E. Orgel).

I will here conclude these general and largely historical remarks, which I hope may have been of some use in providing a background; and I will leave the real modern experts to describe the new knowledge which they have obtained on some of the most important problems raised by the co-ordination compounds.

THE COMPLEX DERIVATIVES OF THE TERTIARY PHOSPHINES AND ARSINES WITH MERCURY AND CADMIUM

By Dr. F.G. Mann, F.R.S.

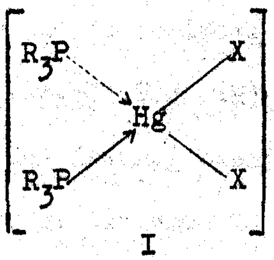
(Cambridge University)

The work now described on the complex derivatives which mercuric and cadmium halides form with tertiary phosphines and arsines had to be stopped in the early stages of the war, and consequently much remains to be done. It has shown however that mercury can give rise to a much greater variety of complexes than hitherto supposed, and that the formation of these compounds is often determined by specific factors.

Mercuric halides can combine with tertiary phosphines and arsines to form compounds belonging to five classes, with the following representative compositions: (A) $[(R_3As)_2HgX_2]$; (B) $[(R_3As)_2(HgX_2)_2]$; (C) $[(R_3As)_2(HgX_2)_3]$; (D) $[(R_3As)_2(HgX_2)_4]$; (E) $[(R_3As)_3(HgX_2)_2]$. In the case of cadmium, only compounds of class A, B and E are formed.

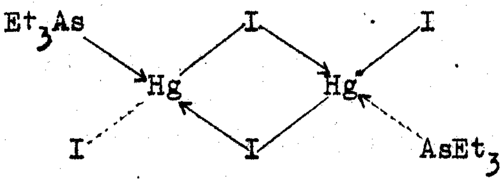
All these products are highly crystalline compounds, readily recrystallised and have sharp melting points. Some of the reactions are very specific, so that, for instance, some complexes can only be prepared with triaryl groups and not tri-alkyl groups: moreover, group D compounds were never obtained with iodides; group E compounds could be prepared with iodides but never with bromides or chlorides. The reason for these limitations is still unknown.

Class A has the two arsine molecules linked to the mercury, which has a tetrahedral configuration.

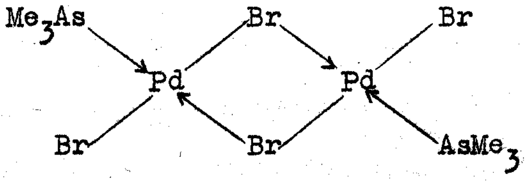


I

Class B is the most frequently occurring type of compound. It has a bridged structure (II), for which Dr. R.C. Evans and Mr. S. Peiser have obtained very considerable X-ray crystallographic evidence. They have shown that the mercury has the tetrahedral configuration, and that the molecule has a centre of symmetry. Apart from the configuration of the metal, these compounds are closely similar to the bridged palladium compounds (III).

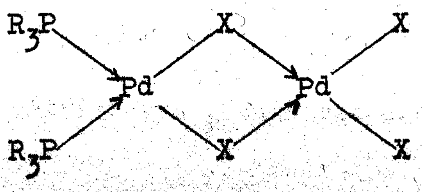


II



III

Theoretically both the mercury and the palladium compounds could exist in the trans and cis forms, and also in a third form in which two phosphine molecules joined to the same metallic atom (IV)



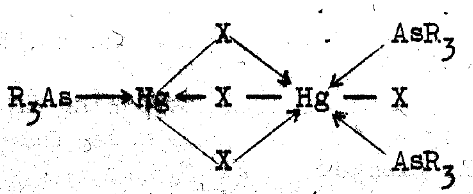
IV

In no case was there evidence that there were mixtures of isomers in the solid state and the compounds were obviously homogenous. Dr. Wells carried out X-ray examination of the palladium compounds and showed them to be planar with a centre of symmetry, and must have the *trans*-symmetric structure. Dipole measurements were carried out by Professor Sidgwick and Dr. Finn and these showed that the moment in solution was zero. There is, therefore, a close correspondence between the mercury and cadmium compounds on the one hand, and palladium compounds on the other.

The triphenylarsine derivatives of the mercuric halides show an interesting gradation in stability. When mercuric chloride was boiled in alcohol even with a large excess of Ph$_3$As, only the bridged Class B compound was formed. In similar circumstances mercuric bromide gives the unbridged compound of Class A, which on attempted recrystallisation from hot benzene gives the bridged derivative of Class B. Mercuric iodide gives solely the compound of Class A, the derivative of Class B being unknown

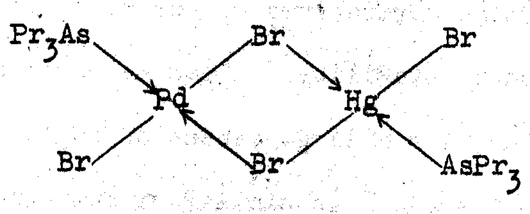
Class C. Compounds of this class were obtained as yellow and white crystals. The two isomers were obviously quite distinct. The yellow crystals may also have the "bridged" structure and were shown by Dr. Evans to have no centre of symmetry. It is possible that this compound has an extended bridge by the insertion of another mercuric halide unit, which would account for the absence of a centre of symmetry. The structure of the white form, however, was extensively investigated by X-ray analysis by R.C. Evans and S. Peiser. It appeared to consist of molecules of Class B alternating with simple HgX$_2$ molecules, the complete arrangement providing a centre of symmetry.

Classes D and E. The structures of compounds of these classes are still unknown. Compounds of Class E are of particular interest, and it is possible that they have the structure (V), with 4- and 6- co-ordinate mercury atoms.



V.

It is of considerable interest to determine to what extent bridged compounds of type (II) and (III) can be prepared with two different metals in the molecule. It is quite possible to make compounds containing both mercury and cadmium by mixing the two parent compounds in equimolecular proportions in solution. The resulting mixed compounds are much less soluble than the parent compounds and have higher melting points. Many attempts were also made to prepare compounds containing two metals of unlike configuration, for example, mercury and palladium. Success was achieved however only in the compound (VI), and in certain mixed tin-mercury compounds.



VI

GENERAL DISCUSSION

Dr. Palmer expressed his particular interest in what Dr. Mann had said in the early part of his talk on the influence of the different halogens, as the halogens are present in the co-ordination complex and the difference of reactivity may be capable of explanation. The case occurred to him which he had recently observed which was less easy to explain, and that was of the anion outside the complex having an influence on the behaviour of the complex. It is unusual for urea to form complexes, but hexa-urea chromic chloride $(Cr(urea)_6)Cl_3$ had been described. The chromic chloride complex cannot be recrystallised even from urea solutions, but if you take the corresponding iodide complex, you can recrystallise from boiling water. The bromide can be recrystallised from cold water. The anion is affecting the behaviour of the complex, but the explanation is not evident.

Professor Sidwick expressed the view that if the compound forms crystals the nature of the halogen will affect the stability of crystal, but he asked if there was any case of this happening in solution. Dr. Palmer could think of no example.

Dr. Mann stated that in his compounds the halogen was forming part of a bridge, and could be partially responsible for the difference in stabilities but that this was not the complete explanation. Cadmium did not behave in exactly the same way as mercury.

Dr. Anderson urged the need for supplementing preparative work by studies of equilibria in solution. Dissociation equilibria of the solutions may be important in deciding behaviour of systems like these. Information can be obtained by X-ray work, but the limitations of this technique make this difficult. He expressed the view that compounds of type E might be lattice complexes of Class B and another group. Here Dr. Mann agreed that until X-ray information is available the structure cannot be decided.

F.H. Burstall urged the use of absorption spectroscopy and asked whether more than four molecules of the mercuric halide ever occurred in one molecule and if there was any limit to the extent to which bridging could be continued. Dr. Mann remarked that there were no definite compounds beyond Class D. The crystals in the earlier classes were hard and well defined but in Class D were becoming definitely less clearly formed.

Dr. Nyholm described an octahedral complex of mercuric chloride with rhodium, which crystallised with benzene of crystallisation. It contained one atom of rhodium to one atom of mercury and was expected to be a bridged compound but X-ray analysis showed that this was not so.

Dr. Chatt added a few words on the number of metal atoms which can take part in a bridged structure, describing the decomposition of ethylene-p-toluidine dichloroplatinum in boiling carbon tetrachloride solution. Ethylene was lost and trans-di-p-toluidine dichloroplatinum separated initially. This was followed by products becoming more red and darker in colour as the reaction proceeded, until finally a product analysing approximately as $CH_3C_6H_4NH_2,.3PtCl_2$ was obtained in small quantity. This was soluble in chloroform so could not contain free platinous chloride. It was difficult to see how so much platinous chloride could be rendered soluble by so little p-toluidine, but if the complex had a bridged structure, and it was difficult to see what else it had, then here we had six metal atoms joined by halogen bridges. He had also prepared a number of bridged platinum complexes exactly analogous to Dr. Mann's palladium complexes and therefore capable of existing in three isomeric forms but again only the trans symmetric forms were found. The decomposition of ethylene-p-toluidine dichloroplatinum did supply a small quantity of an orange compound $(CH_3C_6H_4NH_2)_2Pt_2Cl_4$ which was dimeric and changed in acetone solutions to a pink complex of exactly the same composition, but the quantity obtained was too small to determine whether it was dimeric. If it was then this would be an example of isomerism due to the function of the p-toluidine molecules.

STABILITY CONSTANTS OF CHELATE COMPLEXES

By Prof. G. Schwarzenbach

(Zürich University)

The chemistry of co-ordination complexes has made remarkable progress in the last few years, thanks to the modern systematic investigations of ionic equilibria of solutions containing metallic complexes. Information concerning the free energies of the complex ions and the heat changes of the reactions by which they are formed may be obtained only through such measurements and the data are particularly valuable in that they are neither influenced by the lattice energy of the solid complex salt nor by the counter ion of the complex ion under examination. These measurements have been applied chiefly to those complexes which readily dissociate and reform in solution, rather than to those which have played the principal role in the classical chemistry of complexes and which can be well investigated with the help of preparative methods. In this connection, it may be pointed out that the stability of many of the known complexes of Cr(III), Co(III), Fe(II) etc. is probably due to the slowness of the decomposition and formation reactions rather than to a particularly large free energy of formation.

The idea of studying by equilibria measurements the manifold complex reactions, which can be readily examined at any time from colour and solubility manifestations, is in no way new. Around the turn of the century, such measurements were undertaken by Abegg, Bodländer, Euler and others (Z. phys. Chem. 39, 597 (1902); Euler, Berichte deutschen chem. Gesellschaft 36, 3400 (1903)). These studies, however, never played an important role in the chemistry of complexes, because the measurement technique then used was applicable to only a few metals and also the results were unreliable. The method in exclusive use at the time consisted in the potentiometric determination of the free (not present in complex form) metal cation in the equilibrium mixture by means of an electrode of the elementary metal concerned. The researches were thus restricted to the complexes of those metals which respond normally to their own ionic concentrations chiefly Ag, Hg, Cd, and Zn. The unreliability of the earlier measurements was of course due to the then existing inexact knowledge of solutions of the electrolytes, which failed to take into consideration ion activities or liquid junction potentials.

The impetus to the execution of better measurements came from Jannik Bjerrum ("Metal Ammine Formation in Aqueous Solution" Thesis Kopenhagen, 1941) whose most important work on the ammine complexes of different metals appeared in 1941. He made considerable use of the glass electrode, which McInnes, Dole and others had developed to a precision instrument with which pH-measurements can be effected today in the presence of any metal ion. The displacement, which the protolytic equilibria (I)

$$H^+ + A \rightleftharpoons HA \qquad (I)$$

undergoes on the addition of metal cations, was studied with a view to obtain information about the complex reaction (II).

$$M + n\,A \rightleftharpoons MA_n \qquad (II)$$

This method is quite general in its application so long as the ligand A is a sufficiently strong proton acceptor, which is mostly the case. Besides this most important method, potentiometry with amalgam electrodes (Leden, Dissertation Lund 1943, Fronaeus, Dissertation Lund 1948) (especially for Cu and Cd) as well as optical methods also play their part. The polarographic method is on the other hand only seldom useful for precision measurements (Koryka, Kössler, Coll. des travaux tchécosl. <u>XV</u>, 241 (1950)).

The most surprising result of the first significant series of precision measurements such as are compiled in the work of Bjerrum, was the general conclusion that in complex formation, the different ligands are always added on in steps. One after another of the water molecules of the sheath of hydration of the metal cation in aqueous solution is replaced by the entering ligand.

$$M \longrightarrow MA \longrightarrow MA_2 \longrightarrow MA_3 \ldots\ldots\ldots \longrightarrow MA_i \ldots\ldots \longrightarrow MA_n \qquad (III)$$

The mutual relationship of the individual formation constants of the successive intermediates is interesting in this connection.

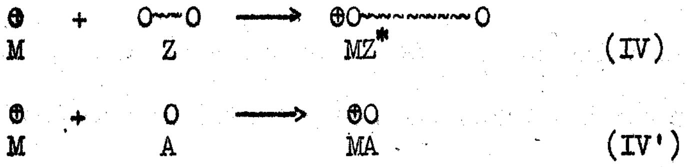
$$q = k_{MA_i} / k_{MA_{i+1}}, \quad \text{where } k_{MA_i} = \frac{[MA_i]}{[MA_{i-1}][A]} \qquad (1)$$

It has been proved that the magnitude of q is of the order that might be expected from statistical computations. By statistical behaviour is meant that the metal cation shows a fixed number of completely identical points of attachment and the ability of a particular point to fix the ligand is in no way influenced by the ligands already existing in the complex. In such a case q is naturally determined simply by the number of occupied and free positions round the central atom, that is by i and n, and sums up to about 2 to 4.

It is true that closer consideration almost always reveals certain deviations from pure statistical behaviour. Thus, the silver ion adds on two molecules of NH_3 or amine almost simultaneously and the intermediate AgA^+ has a lesser stability than that statistically calculated (Bruhlman, Verhoek, Journal American chem. Soc. <u>70</u>, 1401 (1948)). The silver ion tends thus towards a certain degree of symmetry, in which the two existing co-ordination points may be occupied either both by H_2O or both by NH_3. An exactly similar situation arises with the ammonia complexes of zinc, in which case the three intermediates $Zn(NH_3)^{2+}$, $Zn(NH_3)_2^{2+}$ and $Zn(NH_3)_3^{2+}$ appear likewise in smaller concentration in the equilibrium mixture than that statistically expected (J. Bjerrum, loc. cit.). On the other hand, there are also cases known, which, in contrast to simple statistics, involve larger steps, with larger values for q. Such a behaviour is naturally understandable when the ligand is an anion, so that at every stage the charge of the complex is so changed that the following ligand encounters a larger electrostatic repulsion. It is often possible to infer also from the constants of formation that different kinds of points of attachment are present; e.g., in the case of Cd^{2+} four such positions hold the ligands more firmly than two other positions. It is usual then to speak of a characteristic and of a maximum co-ordination number. Similar behaviour is observed with zinc and with mercury and probably also with cobalt (II). A very noteworthy case is that of the addition of iodide ions to Cd^{2+}, since essentially only the complexes CdI^+, CdI_3^- and CdI_4^{4-} appear in the equilibrium mixture while the molecule CdI_2 is present in almost undetectable concentration (Leden, Z. phys. Chem. (A) 188, 160 (1941)). These deviations from statistical behaviour are, however, not very large. The value of q lies almost always between 1 and 10.

After this consideration of complexes with simple ligands A, we may now turn to the chelate complexes, the polydentate partner of which we shall in general denote as Z. It is a universally recognised fact that chelate complexes are in general considerably more stable. The replacement of two molecules of ammonia by ethylenediamine (= en) is almost always associated with a considerable increase in stability. The effect is less when two molecules of ammonia are replaced by trimethylenediamine (pn). Well defined complexes with higher members of the polymethylenediamine series were first prepared only very recently in 1948. Pfeiffer and co-workers (Naturwissenschaften 35, 190 (1948)) described copper complexes with tetra- and hexamethylenediamine (tn and hn): $[Cu(tn)_2][(ClO_4)_2]$ and $[Cu(hn)_2][(ClO_4)_2]$, which were obtained crystalline from alcohol or ether solution. These salts, however, hydrolyse at once as soon as they come into contact with water, which behaviour recalls that of the familiar tetrammine-copper-complex, $[Cu(NH_3)_4]X_2$, in the absence of an excess of ammonia. It appears, therefore, that the formation of 7 or 9-membered chelate rings is not tied up with an essential increase of stability.

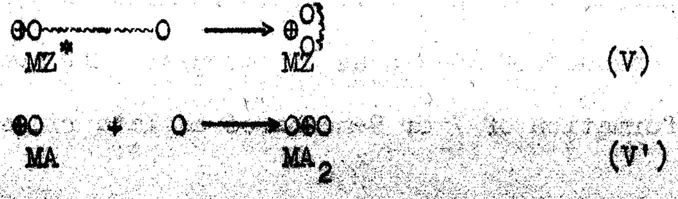
These findings of preparative "complex" chemistry are in complete agreement with the results of equilibria measurements. It was always observed that formation of a 5-membered chelate ring was associated with a larger increase of the complex formation constant and that of a 6-membered ring with a correspondingly smaller increase (H. Irving, this discussion). The only known exceptions up to date are the silver complexes, which we shall discuss later. As is evident from magnetic properties and light absorption the ligands in most chelate complexes are linked to the central atom by the same forces. Special forces come into play only in the case of those chelate complexes which contain a conjugated system of double bonds linking two or more of the ligand atoms within the polydentate partner and available for co-ordination with the central metal atom as e.g. the complexes of acetylacetone, salicylaldehyde, (Calvin and co-workers, J. Amer. chem. Soc., 67, 2003 (1945); 68, 557, 949 (1946)), dipyridyl, etc. With the saturated aliphatic polyamines, however, the only obvious reason for the greater stability of the chelate complex is the smaller entropy decrease accompanying their formation as against that of the complexes with simple ligands. This effect may perhaps be interpreted in the following manner: we imagine the formation of the chelate complex say with a bidentate partner, to take place in two steps IV and V, which may then be compared with the addition IV' and V' of two individual simple ligands:



$$\underset{M}{\oplus} + \underset{Z}{O\sim O} \longrightarrow \underset{MZ^*}{\oplus O\sim\sim\sim\sim O} \qquad (IV)$$

$$\underset{M}{\oplus} + \underset{A}{O} \longrightarrow \underset{MA}{\oplus O} \qquad (IV')$$

The two reactions IV and IV' are undoubtedly accompanied by very similar free energy changes. Whereas it is clear that the equilibrium constant of the tautomerisation reaction V will be much bigger than that of V', if a strainless chelate ring is to be formed.



$$\underset{MZ^*}{\oplus O\sim\sim\sim\sim O} \longrightarrow \underset{MZ}{\oplus\begin{matrix}O\\O\end{matrix}\}} \qquad (V)$$

$$\underset{MA}{\oplus O} + O \longrightarrow \underset{MA_2}{O\oplus O} \qquad (V')$$

A ready comparison of the two reactions V and V' then becomes possible, if we imagine the unco-ordinated ligand atom in MZ^* to be confined to the small space determined by the operation of free rotation round the C-C and the C-N bonds. We may then speak of an apparent ligand concentration (or better, activity a_L) which exists in this small space. For the formation of a strainless chelate ring, the co-ordination points round the central metal atom adjacent to that already occupied must likewise be within this space. The metal cation thus finds itself to a certain extent in a solution of an extraordinarily high ligand concentration ($= a_L$). With the help of this simple hypothesis a relationship between the constants of formation of MZ and MA_2 may be obtained, whereupon the difference of the two logarithms of $k_{MZ} \left\{ \equiv \frac{[MZ]}{[M].[Z]} \right\}$ and $K_{MA_2} \left\{ \equiv \frac{[MA_2]}{[M]\cdot[A]^2} \right\}$ are identical with log a_L not taking account of an important statistical factor. In the cases where a strainless chelate ring can be formed, the increase in the stability in passing from the complex with simple ligands to the corresponding chelate complex should be largely independent of the metal cation. Furthermore, this view makes it perfectly clear that the rise in the stability must rapidly diminish as the number of members of the chelate ring is increased, since the chain between the two ligand atoms is thereby made longer and a_L correspondingly smaller.

Analogous considerations may be applied to the case of complex formation with a polydentate partner. The ligand atoms are here so arranged that pure strainless chelate rings with the same number of members, e.g., 5-membered rings, can form with the result that for every ligand atom with which the polydentate group is further attached by co-ordination with the metal the same increase in stability of the chelate complex should always occur, as is evident from the following equations:

$$\left.\begin{array}{lll} Z = \text{bidentate} & : & \log k_{MZ} - \log K_{MA_2} = \log a_L \\ Z = \text{tridentate} & : & \log k_{MZ} - \log K_{MA_3} = 2.\log a_L \\ Z = \text{quadridentate} & : & \log k_{MZ} - \log K_{MA_4} = 3.\log a_L \end{array}\right)$$

TABLE 1

Logarithms of the Formation Constants of Ammine- Complexes

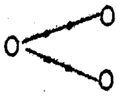
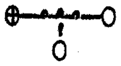
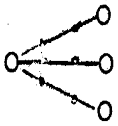
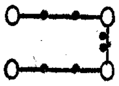
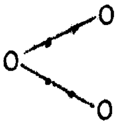
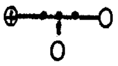
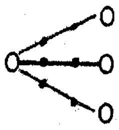
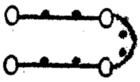
	Cobalt (II)						Nickel (II)					
with A 0	2,1	1,6	1,0	0,7	0,1	-0,7	2,7	2,1	1,6	1,1	0,6	-0,1
with "en" 	5,9		4,8		3,1		7,7		6,4		4,6	
with "den" 	8,1			6,0			10,7			8,2		
with "ptn" 	6,8			?			9,3			?		
with "Hptn" 	4,1		?		?		6,1		?		?	
with "tren" 	12,8				--		14,8				--	
with "trien" 	11,0				--		14,0				--	

TABLE 2

Logarithms of the Formation Constants of Ammine- Complexes

	Copper (II)				Zinc (II)				Cadmium (II)			
with A 0	4,0	3,3	2,7	2,0	2,2	2,25	2,3	2,0	2,6	2,0	1,4	0,9
with "en" 	10,7		9,3		5,9		5,2		5,6		4,6	
with "den" 	16,0			5,0	8,9			5,5	8,4			5,4
with "ptn" 	11,1			9,0	6,7			?	6,5			?
with "Hptn" 	8,8		7,3		4,3		?		4,7		?	
with "tren" 	18,8				14,6				12,3			
with "trien" 	20,5				11,8				10,7			

Tables 1 and 2 give the stability of a series of chelate complexes (Schwarzenbach, Prue, Helv. Chimica Acta 33, 947, 963, 974, 985, 995 (1950)) showing the logarithm of the individual constants of formation of the complexes with ammonia (= A) and the following polyamines:

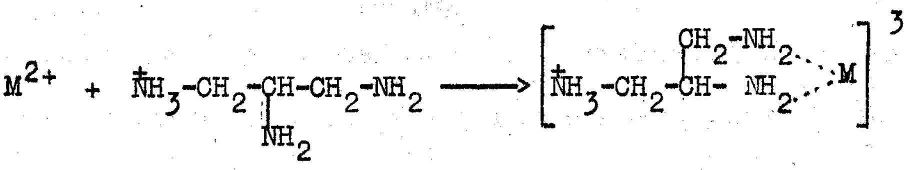
en = $NH_2-CH_2-CH_2-NH_2$, den = $NH(CH_2-CH_2-NH_2)_2$
ptn = $NH_2-CH(CH_2-NH_2)_2$, tren = $N\equiv(CH_2-CH_2-NH_2)_3$
trien = $NH_2-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-NH_2$

Thus, the figures of the first horizontal row stand for $\log k_{MA}$, $\log k_{MA_2}$, $\log k_{MA_3}$ etc. where $k_{MA_i} = \frac{[MA_i]}{[MA_{i-1}]\cdot[A]}$

In the second horizontal row are recorded the logarithms of the following constants:

$$k_{M(en)} = \frac{[Men]}{[M]\cdot[en]}, \quad k_{M(en)_2} = \frac{[M(en)_2]}{[Men][en]} \quad \text{etc.}$$

The fifth horizontal row contains the constants of formation of a hydrogen containing complex, which has a proton in addition to the metal cation and the triamine molecule ptn. The value shown is proportional to the free energy change of the following reaction:



$$M^{2+} + \overset{+}{N}H_3-CH_2-\underset{\displaystyle NH_2}{CH}-CH_2-NH_2 \longrightarrow \left[\overset{+}{N}H_3-CH_2-\overset{\displaystyle CH_2-NH_2\cdot\cdot}{CH}-\,NH_2\cdot\cdot\cdot M\right]^{3+} \qquad \text{(VI)}$$

Of the two possible modes of formulation for the complex $M(Hptn)^{3+}$, that given with the 5-membered chelate ring is of course more likely than the one with a 6-membered ring (wherein the middle amino group carries the proton) and in fact there exists a structural proof for such a complex (Mann, J. chem. Soc., 129, 2681 (1926).

The logarithms of the "gross-formation" constants, K_{MA_i}, to be inserted in equation (2) are obtained by summation of the successive figures of the first horizontal row:

$$\log k_{MA_i} = \sum_{i=1}^{i=i} \log k_{MA_i}, \quad \text{where } k_{MA_i} = \frac{[MA_i]}{[M]\cdot[A]^i} \qquad (3)$$

The results of the measurements

Nickel: We shall begin the discussion of the results of measurements with Ni^{2+}, for which the characteristic co-ordination number in respect of amino nitrogen is known with certainty to be 6. The stability increase (= Δ) on replacement of the first two ammonia molecules by "en" amounts to 2.9 units, that on replacement of the third and fourth A-molecules by a second "en"-molecule is, however, 3.7 and finally replacement of the fifth and sixth A-molecules by a third "en"-molecule gives a value as high as 4.1. That the energy gain through chelation increases with the number of entering chelate groups is also observed with Co, Cu, and Cd, but not with Zn. An analogous increase is also observed on the entry of the second "den"-molecule as against the first, provided of course that this second molecule has still three positions round the metal available for co-ordination. In passing from NiA_3 to Ni(den) we obtain a stability increase of Δ = 4.3, and, therefore, about 1.5 times the value of the difference for $NiA_2 \longrightarrow Ni(en)$, whereas by equation (2) the value should be doubled. Evidently a small ring strain is beginning to be felt here. The triamine "ptn" with Δ = 2.9 is much worse than the triamine "den". The use of all 3 amino groups of "ptn" as co-ordination partners must naturally cause considerable strain. And yet $k_{Ni(ptn)}$ being essentially larger than $k_{Ni(en)}$ shows that in effect all three amino groups of the triamine are attached to the metal and not just two. One of these groups can, however, readily break off and add on a proton, thus accounting for the appearance of the hydrogen containing complex $Ni(Hptn)^{3+}$ in the equilibrium mixture. In the case of diethylenetriamine, acidification does not give rise to a corresponding $Ni(Hden)^{3+}$ as intermediate but the whole triamine molecule is detached in one step and converted into the triammonium cation H_3den^{3+}, as soon as the necessary low pH value is attained. The two tetramines "tren" and "trien" form very stable Ni-complexes. The increase in the conversion $NiA_4 \longrightarrow Ni(tren)$ amounts to 7.3 and the corresponding one for the "trien" is 6.5 units. These correspond to about 2.5 times the value of the stability increase for $NiA_2 \longrightarrow Ni(en)$ which is not much less than that predicted by equation (2). Undoubtedly then, the strain involved in the formation of the three chelate rings is only negligible.

Copper: The constants of complex formation found for Cu are also easy to understand. The differences on replacement of the first two and of the last two ammonia molecules by "en" amount to 3.4 and 4.6 respectively, and are thus of a similar magnitude as for Ni. The stability increase in the conversion $CuA_3 \longrightarrow Cu(den)$ is 6.0 units and so not much less than double the value prescribed by equation (2). The gain of free energy on the addition of a second molecule of triamine: $M(den) \longrightarrow M(den)_2$ is only about 1/3 that for the co-ordination of the first molecule: $M \longrightarrow M(den)$, because, in the particle $Cu(den)^{2+}$, only one co-ordination position of the metal is still free. The adduct with triaminopropane Cu(ptn) is here scarcely more stable than the complex Cu(en), which shows that an almost free amino group must still be present. This observation is in compliance with the considerable basicity of Cu(ptn), which already at pH 7, changes to the hydrogen containing complex $Cu(Hptn)^{3+}$. The comparison of the two tetramine complexes $Cu(tren)^{2+}$ and $Cu(trien)^{2+}$ is also interesting. The former is considerably less stable than the latter, which is easy to understand when one recalls that Cu(II) forms complexes with a square configuration, for the four corners of a square can be very easily "wrapped up" with the four nitrogen atoms of the straight chain tetramine "trien" but require the use of some force to do the same with the nitrogen atoms of the branched chain "tren". It is remarkable, however, that Cu(tren) has nevertheless a considerably bigger constant of formation than the triamine complex Cu(den). Thus it appears that all the four co-ordination points of Cu are "satisfied" by the "tren" molecule, in spite of steric hinderance. Evidently then, the co-ordination polyhedron of the metal cation can be rather strongly deformed without much adverse effect on the stability of the complex.

Zinc: We may now turn to Zn for which metal it is established that the ligands lie tetrahedrally round it. The slight stability increase in the conversion: $ZnA_2 \longrightarrow Zn(en)$ is remarkable. A ring strain is probably already in existence here. The stability of Zn(den) is, in comparison with that of ZnA_3, also rather small, while that of Zn(ptn) is unlike the case of the other metals. On the other hand it is surprising to observe the large affinity of Zn for the tetramine "tren" and the big difference between the constants of formation of Zn(tren) and Zn(trien) amounting to as much as 2.8 units. In this respect Zn differs radically from Cu which prefers "trien" to "tren".

Cadmium: Similar to the behaviour of Zn is that of Cd. Here again we observe a similar "antipathy" towards "en", "den" and "trien" and a relatively large formation constant for Cd(tren). Further, it is remarkable that the stability gain on the entry of the first molecule "en" is particularly small while that on entry of the second molecule resulting in $Cd(en)_2{}^{2+}$, is much larger. This may be attributed to the fact that the two ligands in CdA_2 lie opposite to one another, as in the diammonia derivative of silver $AgA_2{}^{+}$, and of mercury $HgA_2{}^{2+}$, so that a considerable ring strain is brought into existence by "en", bridging over these two positions. Subsequent addition of the second molecule of "en", then perhaps causes a rearrangement to a tetrahedron and with it a corresponding relief of the ring strain.

Cobalt shows a behaviour towards the polyamine molecules that places it between zinc and nickel. The effect of chelation with "en" is larger than that for Zn but smaller than that for nickel. Similar to Zn and Cd, cobalt also shows a preference for the tetramine "tren" over the tetramine "trien".

In concluding, we may compare the hydrogen containing complex M(Hptn) with the complex M(en).

TABLE 3

Stability Difference between the Complexes with "en" and with "Hptn".

$$\Delta = \log K_{M(en)} - \log K_{M(Hptn)}$$

	Co••	Ni••	Cu••	Zn••	Cd••	Ag•
Δ =	1,8	1,6	1,9	1,6	0,9	1,8

In both, the same 5-membered chelate ring must be present. But the hydrogen complexes are obviously less stable because of the electrostatic repulsion between the metal cation and the ammonium group and it is noteworthy that the difference of the logarithms of the two formation constants varies only slightly from metal to metal, as shown by Table 3. Only cadmium behaves anomalously, due again to the low value of the stability constant of Cd(en). It is quite possible that the hydrogen complex does not possess here the structure given in equation VI, but that this time a 6-membered chelate ring is involved which can span better the bridge between the two opposite lying co-ordination positions. In such a case, the proton would naturally be carried by the middle amino group.

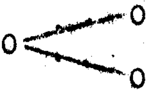
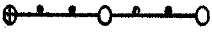
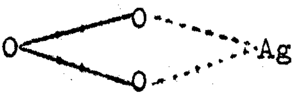
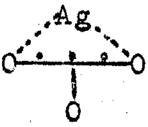
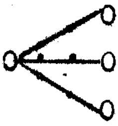
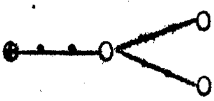
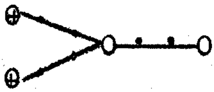
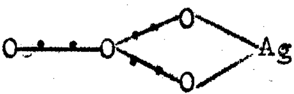
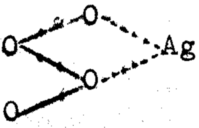
Silver: Table 4 gives the formation constants of the Ag- complexes. The silver ion behaves differently from all other metals studied in that $Ag(en)^+$ is less stable than AgA_2 and $Ag(pn)^+$ is more stable than $Ag(en)^+$. This is most likely due to the fact that the two co-ordination positions of Ag^+ lie on opposite sides. This idea limits the ease of detachability of an amino group and the addition of a proton to the detached group thus accounting for the existence of the hydrogen containing complexes $Ag(Hen)^{2+}$ and $Ag(Hpn)^{2+}$. In the case of "pn" $Ag_2(pn)^{2+}$ could also be detected in the equilibrium mixture.

The stability of silver complexes is hardly enhanced with the triamines "den" and "ptn". With the tetramines, both $Ag(tren)^+$ and $Ag(trien)^+$ are of about equal stability and their free energies are not much larger than that of $Ag(NH_3)_2^+$. Two hydrogen containing complexes and a di-silver complex is detectable in each case.

The above facts can be explained if it is assumed that the silver cation adds on only two basic nitrogen atoms and that these two co-ordination positions are opposite one another. Only a polymembered atom chain can then span the arc between these two positions, in which case, of course, a_L will not be large and, therefore, the chelation will not be accompanied by any particular energy gain. Small chelate rings, such as with "en" and "pn" can, nevertheless, be built, without much ring strain. It appears then what the valency angle (180°) between the directions of the two ligands can be relatively easily "compressed".

TABLE 4

Logarithms of the Formation Constants of Silver-Ammine Complexes

NH_3	0	3,2	3,8
en		5,2	(2,2)
Hen		2,0	?
pn		5,8	
Hpn		2,7	
Agpn		1,1	
den		6,1	
Hden		3,2	
Agden		1,5	
ptn		5,7	
Hptn		3,4	
Agptn		1,0	
tren		7,8	
Htren		5,7	
H_2tren		3,3	
Agtren		2,4	
trien		7,6	
Htrien		5,7	
H_2trien		2,8	
Agtrien		2,5	

THE STABILITY OF CO-ORDINATION COMPOUNDS IN AQUEOUS SOLUTION AND THE VARYING STRENGTHS OF METAL-LIGAND BONDS

By Dr. H. Irving

(Oxford University)

Introduction

Until recently, most studies of co-ordination compounds have been carried out largely with solid substances and the problems arising out of their differing stabilities - their varying ease of formation, decomposition or disproportionation - have been complicated by the very fact that solid lattices rather than individual molecules have been under review. Thus extensive studies of molecular volume have served chiefly to introduce misleading distinctions between normal and penetration lattices (R.W. Parry, Chem. Reviews, 1950, 46, 507) whilst the tensimetric measurements of Biltz and his school have really thrown less light on the actual stabilities of co-ordination compounds than on the complications arising out of their aggregation into crystal lattices. Brown and his school in America have secured useful thermodynamic data from studies of the dissociation of compounds of the type $X_3B \longleftarrow Nabc$ and established the importance of steric factors in these simple cases of co-ordination, but the data are necessarily limited to certain highly specialised types of compounds. Now some of our most valuable knowledge of co-ordination compounds derives from studies of dipole moments and optical activity. But these are essentially properties of the individual molecule in solution, and it is to solution chemistry that we must turn for data of greater variety and more quantitative character.

Solution Chemistry

The work of N. Bjerrum on the chromium-thiocyanate complexes and that of his son J. Bjerrum summarised in his book "Metal Ammine Formation in Aqueous Solution" (Copenhagen, 1941) gave a tremendous impetus to solution chemistry for it demonstrated that it was experimentally possible to study and measure the equilibrium constants of complexes existing together in various proportions in aqueous solution. Thus in an ammoniacal solution of copper sulphate we have to reckon with (at least) five species of formulae $[Cu(NH_3)_n]^{++}$ (n = 0, 1,2,3, and 4), with the possibility of $[Cu(NH_3)_5]^{++}$ at high ammonia concentrations. If the formation of the complex ML_N from the ion M and the ligand L (charges are omitted for the sake of generality) proceeds through a number of stages

$$M + L \rightleftharpoons ML; \quad ML + L \rightleftharpoons ML_2; \; \ldots\ldots \; ML_{n-1} + L \rightleftharpoons ML_n \; \ldots\ldots,$$

and we define $k_n = [ML_n] / [ML_{n-1}][L]$, we are often able to obtain accurate values for the complexity constants (formation or stability constants) of the individual complexes (n = 1,2 ..... up to N, where N is the maximum or co-ordination number). Clearly $[ML_N] / [M][L]^N$ = K_N (the overall stability constant) = $k_1k_2k_3 \ldots k_N$.

It is important to emphasise that by the methods of solution chemistry, we are able to study quantitatively the stability of individual members of groups of closely related and very similar compounds, free from the confusing issues of lattice energies. Moreover, we can even make quantitative studies of complexes which cannot be isolated in a pure state - inasmuch as they can exist only in solution and in equilibrium with other complexes. It cannot be too strongly emphasised that a knowledge of the composition of the solid phase existing in equilibrium with a solution is not sufficient to give unambiguous evidence as to the nature and composition of the substance or substances existing in solution. From the fact that common salt has the composition NaCl we do not conclude that the sodium and chloride ions are unhydrated in a saturated aqueous solution! A more subtle illustration of the same point is afforded by ferrous ions and 2-methyl-1:10-phenathroline (mpn), for though the tris-complex $[Fe(mpn)_3](ClO_4)_2$ separates readily from aqueous solutions, the solution in equilibrium with this substance can be shown to contain negligible amounts of this tris-complex, for $[Fe(mpn)]^{++}$ is the predominant species with some $[Fe(mpn)_2]^{++}$ and excess methylphenanthroline.

Since the war many studies of equilibria involving co-ordination compounds have been published and a great variety of techniques have been explored e.g. hydrogen, glass and metal electrodes, polarographic, partition and spectrophotometric procedures and the use of ion-exchange resins. Not all the results are of equal reliability, but there are surely enough data to make it worth while seeing whether any regularities are detectable, and whether it is still premature to hazard any generalizations.

Free-Energy Changes

Experimental measurements lead to values of equilibrium (stability or complexity) constants k_n at a given temperature. From these the free-energy change in the relevant reaction is given by the familiar equation $F\Delta = -2.303RT \log {}_{10}k_n$.

$\text{Log.}_{10}k_n$ is thus a measure of the free-energy change in any stage of a stepwise complexing reaction and Bjerrum himself sought for regularities in the values of log k for the successive additions of a ligand molecule to a central ion. Table I shows some typical data:

TABLE I

	log k_1	log k_2	log k_3	log k_4	log k_5	log k_6
Cr^{+++} + $6SCN^-$	3.1	1.7	1.0	0.3	-0.7	-1.6
	(2.3)	(1.3)	(0.9)	(0.4)	(-0.3)	(-0.8)
Cu^{++} + $5NH_3$	4.15	3.50	2.89	2.13	-0.52	
	(3.55)	(3.32)	(3.07)	(2.73)		
Ni^{++} + 3En	7.66	6.40	4.55			
	(6.88)	(6.30)	(5.43)			

(The figures given in brackets represent log k_n values corrected for the statistical effect q.v.)

It is easy enough to deduce that, whether the nature of the bond between M^{n+} and L (or L^-) is purely electrostatic, purely covalent, or of hybrid character, each successive ligand ought to be attached with decreasing affinity, i.e. $k_n > k_{n+1}$. This is, in fact, what is normally found. However, the same steady decrease in the value of successive stability constants would also be anticipated from the operation of the statistical effect (Bjerrum, loc. cit.) which takes into account the differences in the number of equivalent ways in which a ligand can be attached or removed respectively from the complex ML_n. Thus in the case of the octahedral thiocyanate complexes of chromium the first ligand can go on (i.e. replace water) in 6 ways but can be detached in only one. On purely statistical grounds therefore, the relative values of the successive constant should be related to one another as $\frac{6}{1} : \frac{5}{2} : \frac{4}{3} : \frac{3}{4} : \frac{2}{5} : \frac{1}{6}$, i.e. $\log k_1/k_2 = \log k_5/k_6 = 0.38$; $\log k_2/k_3 = \log k_4/k_5 = 0.27$; $\log k_3/k_4 = 0.25$. The experimental ratio $\log k_1/k_2 = 3.1 - 1.7 = 1.4$ is too high by the amount 0.38 and, but for the statistical effect, there would only be a 10-fold difference between the affinity of attachment of the first and second thiocyanate ion. The appropriate correction has been made for this and for all the other data quoted and it is clear that there still remains an effect not statistical in origin, even when allowance has been made for any electrostatic interaction effects where charged ions are used as ligands. This *residual effect* (which has unfortunately been termed the "rest effect" by Bjerrum) is seldom large in magnitude and in the case of some systems (e.g. silver and zinc and mercury with some amines) appears to be negative. Bjerrum concludes that it is not really a significant index of specific effects in co-ordination since "it generally shows slight variation within one and the same system" and "to a great extent it is independent of the magnitude of the complexity constant of the system". In his view (*loc. cit.* p. 58) in the main "metal ammine formation proceeds statistically" a conclusion which would appear to deny the possibility of specific influences due to particular metal ions or particular ligands and to relegate this important source of data on the nature and behaviour of co-ordination compounds to an exercise in statistics. It cannot be thought that Bjerrum really contemplated such a sterile hypothesis and in the following sections it is proposed to show that the existing data is capable of a much more fruitful if more speculative interpretation.

Entropy and Heat of Formation

Log k_n is a measure of the free energy change when a ligand molecule becomes attached to the atom M in which process one or more water molecules are presumably displaced. It is not, of course, a direct measure of the heat of formation of the M - L bond (or more accurately the difference in the heats of formation of M - L and $M\text{-}H_2O$) since $\Delta F = \Delta H - \Delta S.T.$ Very little exact information is available concerning the sign and magnitude of entropy effects in the formation of complex compounds. Even that shown in Table II (which shows the affinity of a proton for a neutral basic ligand) is of very unequal

TABLE II

Reaction of a Proton with a Neutral Molecule

Ligand	ΔF	ΔH	ΔS
Ø. $CH_2.NH_2$	-12,777	-13,097	- 1.0
$HO.CH_2CH_2.NH_2$	-12,882	-12,070	+ 2.7
Ø.NH_2	- 6,265	- 7,276	- 3.4
-Picoline	- 8,210	- 6,095	+ 7.0
Pyridine	- 7,234	- 4,721	+ 8.4
NH_3	-12,562	-12,400	+ 0.5
$CH_3.NH_2$	-14,550	-13,100	+ 4.5
$(CH_3)_2.NH$	-14,750	-12,000	+ 9.0
$(CH_3)_3N$	-13,425	- 9,000	+14.3
$NH_2.CH_2CH_2NH_2$	-13,620	-13,100	+ 1.8
$C_2H_5.NH_2$	-14,900	-14,000	+ 3.0
iso-Butylamine	-14,800	-13,500	+ 4.3
$NH_2.C_2H_4.NH.C_2H_4.NH_2$ = "dien"	-13,800	-11,300	+ 8.3
"Trien"	-13,850	- 9,970	+13.1

Reaction is $H^+ + L \rightleftharpoons (HL)^+$; data obtained from the dissociation constants of onium ions.

reliability and in common with that of Table III it is often based on measurements of equilibrium constants at two temperatures differing by no more than 10°, frequently carried out by different authors, and even by different methods.

TABLE III

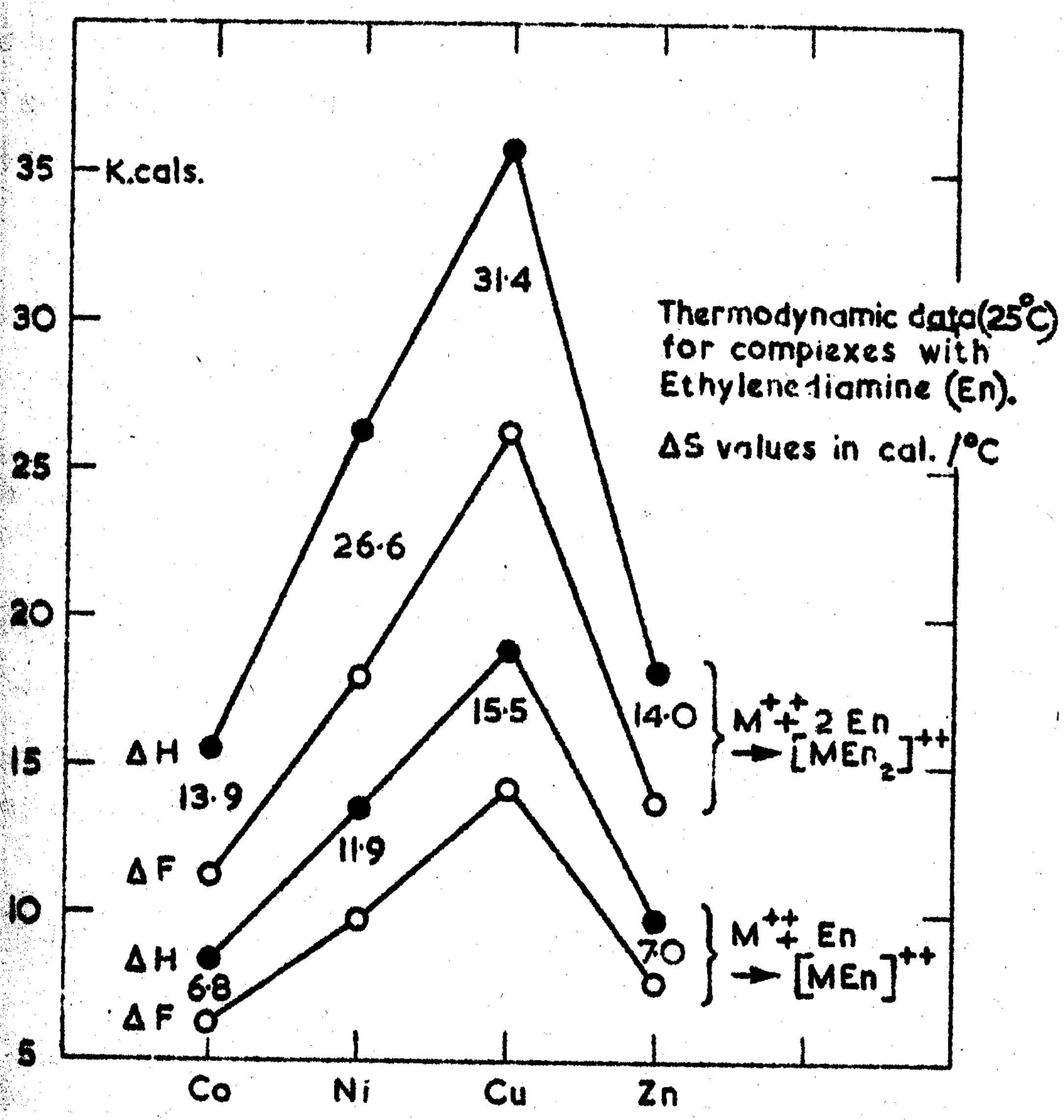
Reaction of Cations with Neutral Molecules

Reaction	ΔF	ΔH	ΔS
Cu^{++} + $4NH_3$	-17,700	-19,700	- 7.0
Zn^{++} + $4NH_3$	-13,300	-13,500	- 2.0
Cu^{++} + en	-14,240	-18,920	-15.5
Cu^{++} + 2en	-26,270	-35,750	-31.4
Zn^{++} + en	- 7,663	- 9,830	- 7.0
Zn^{++} + 2en	-13,810	-18,080	-14.0
Ni^{++} + en	- 9,870	-12,590	-11.9
Ni^{++} + 2en	-18,000	-26,170	-26.6
Co^{++} + en	- 6,320	- 8,380	- 6.8
Co^{++} + 2en	-11,380	-15,600	-13.9
Ag^{+} + $2NH_3$	-10,000	-13,300	-11.0
	- 9.857	-13,400	-11.9
Ag^{+} + pyridine	- 2,820	- 4,700	- 6.3
Ag^{+} + γ-picoline	- 3,130	- 4,700	- 6.3
Ag^{+} + α-picoline	- 3,100	- 4,200	- 3.7
Ag^{+} + lutidine	- 3,400	- 4,700	- 4.3
Ag^{+} + $HO.C_2H_4.NH_2$	- 4,310	- 5,200	- 2.7
Ag^{+} + *iso*-butylamine	- 4,660	- 6,250	- 5.3
Ag^{+} + $C_2H_5.NH_2$	- 4,660	- 6,259	- 5.3
Ag^{+} + benzylamine	- 4,500	- 6,200	- 5.8

Data for transition metals and ethylenediamine by Irving and Williams (unpublished): the rest from various sources.

Only the most tentative conclusion, *viz.* that entropy terms do not in general exert any profound influence on the magnitude of free energy changes in such systems, can legitimately be drawn. Some data of greater accuracy shown graphically in Figure 1 for complexes of ethylenediamine and four divalent ions of the first transition series show that there is a certain parallelism between the magnitude

FIGURE I

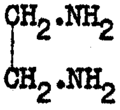
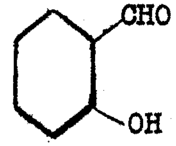
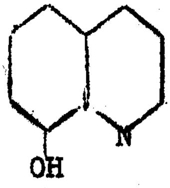
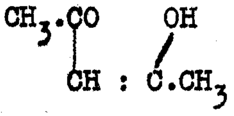
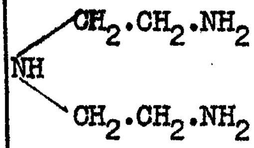

35
30
25
20
15
10
5
K.cals.
Thermodynamic data(25°C) for complexes with Ethylenediamine (En).
ΔS values in cal. /°C
31·4
26·6
13·9
14·0
15·5
11·9
6·8
7·0
ΔH
ΔF
ΔH
ΔF
M++ + 2 En → [MEn2]++
M++ + En → [MEn]++
Co
Ni
Cu
Zn

of entropy and free energy changes so that the order of increasing affinity Co < Ni < Cu > Zn which holds for the attachment of one or two molecules of ligand remains unaltered when the differential heats of formation are being considered. For lack of sufficient information concerning the magnitude of entropy effects in all the remaining metal-ligand systems the following discussion is restricted to considerations of the value of the free-energy changes as measured by log k_n. As it is not always certain what correction ought to be applied for the magnitude of the statistical effects (or whether it is justifiable to introduce them at all in many cases) only uncorrected experimental values of k_n will be employed.

Relationships between the values of log k_n for a given system ML_n.

Consider the stability constants k_n for a series of complexes ML, ML_2 ... formed by the same metal and a given ligand. We have seen that, whatever its actual value may be, k_n may be expected to be numerically greater than k_{n+1}, i.e. it becomes progressively harder to add additional ligand atoms or groups to a central atom. Now examination of Table IV shows that the greater the absolute value of k_1, the greater the relative value of k_1/k_2. This is equivalent to saying that if the first ligand is bound with high affinity (large log k_1) there is proportionately less tendency for the attachment of a second ligand (relatively small log k_2) so that the difference $\Delta 1,2 = \log k_1 - \log k_2$ will increase as log k_1 increases. This generalisation appears to hold good for a variety of metals and a number of different types of ligand. The abnormally high value of $\Delta 1,2$ for copper and diethylenediamine is clearly due to the low value of k_2. One molecule of this amine forms two chelate rings and occupies three of the four co-ordination positions round the Cu^{++} ion which of course forms 4 planar dsp^2 bonds at right-angles. The second molecule can only be attached strongly through one nitrogen atom to the remaining corner, and chelate rings can only be formed, if at all, by weak bonds through orbitals at right angles to the plane of the original chelate rings: k_2 is thus anomalously small. A similar effect is seen in the attachment to copper of a third molecule of

TABLE IV

		Mn	Fe	Co	Ni	Cu	Zn
 $\begin{array}{l} CH_2.NH_2 \\ \vert \\ CH_2.NH_2 \end{array}$	log k_1	2.73	4.28	5.89	7.66	10.55	5.71
	log k_2	2.06	3.25	4.83	6.40	9.05	4.66
	Δ1,2	0.67	1.03	1.06	1.26	1.50	1.05
	log k_1			1.99	2.67	4.15	2.37
NH_3	log k_2			1.51	2.12	3.50	2.44
	Δ1,2			0.48	0.55	0.65	-0.05
	log k_1	3.73	4.22	4.67	5.22	7.40	4.50
	log k_2	3.06	3.40	3.63	3.97	5.90	3.60
	Δ1,2	0.67	0.82	1.04	1.25	1.50	0.90
	log k_1		9.83	10.91	11.65	15.0	10.91
	log k_2		9.01	9.90	10.35	14.0	9.90
	Δ1,2		0.82	1.01	1.30	1.0	1.01
	log k_1			6.30	6.82		
	log k_2			4.88	5.24		
	Δ1,2			1.42	1.58		
	log k_1			8.1	10.7	16.0	8.9
	log k_2			6.0	8.2	5.3	5.5
	Δ1,2			2.1	2.5	10.7	3.4

ethylenediamine: this is so feeble that k_3 is very small and Δ 2,3 exceptionally large as compared with the values for neighbouring transition metals:

		Mn	Fe	Co	Ni	Cu	Zn
$CH_2.NH_2$ $CH_2.NH_2$	log k_2	2.06	3.25	4.83	6.4	9.31	5.15
	log k_3	0.88	1.99	3.10	4.55	-1.0	1.86
	Δ 2,3	1.18	1.26	1.73	1.85	10.3	3.30

The operation of steric effects of a somewhat different kind is illustrated by data in Table V. C-alkylation of ethylenediamine does not greatly effect the stability of the resulting copper chelate complexes. On the other hand, N-alkylation makes it more difficult to attach the second chelate ring (as can be seen readily from a model) so that k_2 is lower than would be expected and Δ 1,2 unexpectedly high. Even the addition of the first molecule of symmetrical dimethylethylenediamine is less readily effected than the addition of the first molecule of ethylenediamine (whether to Cu or Ni) although these two amines have almost identical proton-binding capacity and hence presumably a similar tendency to donate electrons to the central copper ion. But it must not be forgotten that the copper ion is originally hydrated and in chelation small water molecules are being displaced by substituted amines of varying greater bulk.

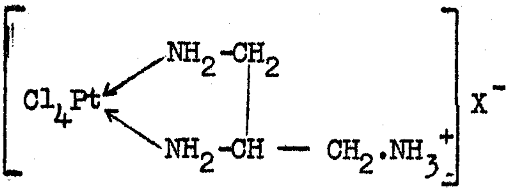
TABLE V

Ligand	Copper Chelates			pK of base
	log k_1	log k_2	Δ 1,2	
$NH_2CH_2.CH_2.NH_2$	10.55	9.05	1.5	10.08, 7.27
$NH_2.CH.CH_2.NH_2$ CH_3	10.58	9.10	1.48	10.06, 7.25
$NH.CH_2.CH_2.NH$ CH_3 CH_3	9.69	6.65	3.04	10.06, 7.28
$NH_2.CH_2.CH_2.N(CH_3)_2$	9.23	6.73	2.50	9.53, 6.63
$NH_2.CH_2.CH_2.N(Et)_2$	8.17	5.55	2.62	10.02, 7.07
	Nickel Chelates			
$Me.NH.CH_2.CH_2.NHMe$	6.67	3.85	2.82	10.06, 7.28
$NH_2.CH_2.CH_2.NH_2$	7.66	6.40	1.26	10.08, 7.27

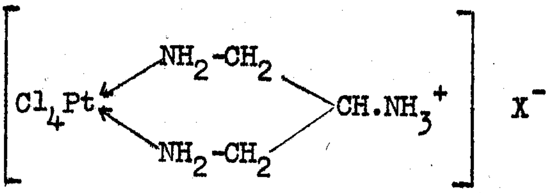
The stability of 5- and 6- chelate rings

In passing it is not without interest to comment on the relative stability of chelate rings of 5- or 6-members. The former have always been assumed to be the stabler, but the evidence has been far from satisfactory. One line of argument rests on the apparently greater "difficulty" of making co-ordination compounds with 1:3-diaminopropane as compared with ethylenediamine - but the evidence is purely qualitative and may merely reflect differences in the kinetics of reaction rather than the position of ultimate equilibrium. Another line of argument is an extrapolation from the behaviour of amines $NH_2(CH_2)_n.NH_2$ with n larger than three which give amorphous or polynuclear or more or less basic complexes with metal ions; but the reason for this is not to be sought solely in the potentially lower stability of multi-membered chelate rings.

So far as the amine triaminopropane is concerned, Dr. Mann produced definite evidence in 1926 that in chelating to platinum a 5-ring was formed rather than a 6-ring, for of the possible products I and II only the former should be resolvable into optically active forms, a result which was effected experimentally.



(I)



(II)

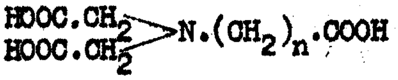
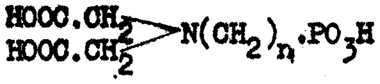
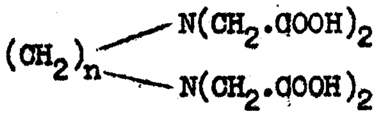
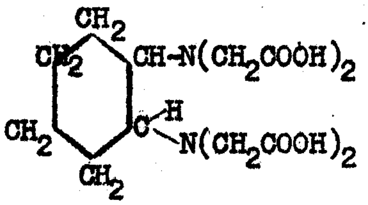
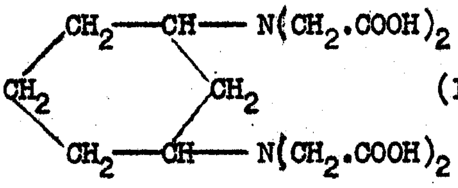
Evidence of a very different kind is now available for it has recently been possible to measure the actual stabilities of a number of chelate rings of 5- and 6-members respectively in which the ring enlargement is a result only of introducing a $-CH_2-$ group. Thus despite the greater basic strength of diaminopropane $NH_2.CH_2.CH_2.CH_2.NH_2$ as compared to ethylenediamine $NH_2.CH_2.CH_2NH_2$, the first chelate ring attached to copper is nearly ten times less stable and the effect is even more pronounced for the attachment of the second chelate ring. Other data presented in Table VI shows that for amino-acids and for simple dicarboxylic acids there is quantitative evidence of the greater stability of the 5-membered ring.

TABLE VI

Ligand	pK_{BH^+}	$pK_{BH_2^{++}}$		$\log k_{CuB^{++}}$	$\log k_{CuB_2^{++}}$	1,2
$NH_2(CH_2)_n.NH_2(B)$						
n = 2	9.87	7.17	2.01	10.55	9.05	1,5
n = 3	10.72	8.98	1.74	9.77	7.17	2,6
$NH_2.(CH_2)_nCOOH(HX)$				$\log k_{CuX^+}$	$\log k_{CuX_2}$	1,2
n = 1	2.25	9.85		8.5	6.9	1,6
n = 2	3.6	10.36		7.15	5.65	1.5
$HOOC.(CH_2)_n.COOH(H_2A)$	pK_{AH^-}				$\log k_{CuA_2}$	
n = 0	4.29				8.4	
n = 1	5.67				8.16	

That this effect is not confined to chelate rings attached to copper, is shown by data for amino acids and diamines chelated to nickel and zinc (not quoted here) and from data obtained by Prof. Schwarzenbach for various alkaline earth metals, given in Table VII.

TABLE VII

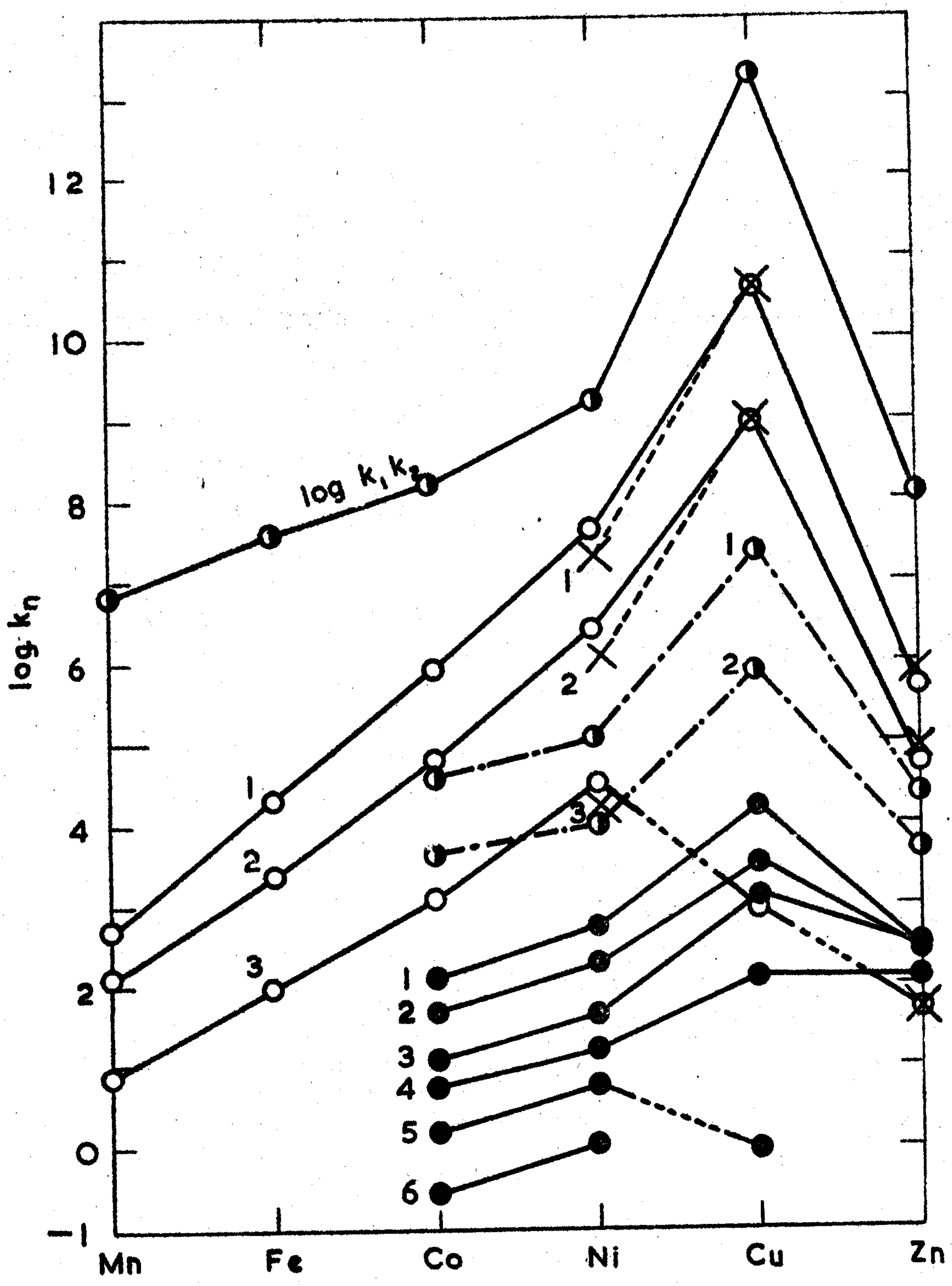
		H	Mg	Ca	Sr	Ba
 $\begin{matrix}HOOC.CH_2\\HOOC.CH_2\end{matrix}>N.(CH_2)_n.COOH$	n = 1	9.73	5.41	6.41	4.98	4.82
	n = 2	9.66	5.28	5.04	3.87	3.40
	$\Delta_{1,2}$	0.07	0.13	1.37	1.11	1.42
 $\begin{matrix}HOOC.CH_2\\HOOC.CH_2\end{matrix}>N(CH_2)_n.PO_3H$	n = 1	10.76	6.28	7.18	5.59	5.35
	n = 2	10.46	6.33	5.44	4.10	3.64
	$\Delta_{1,2}$	0.30	-0.05	1.74	1.49	1.71
 $(CH_2)_n\begin{matrix}N(CH_2.COOH)_2\\N(CH_2.COOH)_2\end{matrix}$	n = 2	10.26	8.69	10.59	8.63	7.76
	n = 3	10.27	6.02	7.12	5.18	4.24
	$\Delta_{2,3}$	-0.01	2.67	3.47	3.45	3.52
 (III)	III	11.70	10.3	12.50		
 (IV)	IV	10.91	4.64	4.77		
	$\Delta_{III,IV}$	0.79	5.7	7.73		

In setting up models of the complexes of copper with 1:3-diaminopropane (where the 6-membered chelate rings cannot be coplanar) there appears to be the possibility of cis-trans isomerism. Closer examination shows that the isomers will not preserve their identity for the six-ring, like that of cyclohexane, appears to be completely strainless.

The "Natural Order" of Stabilities of the Transition Metals

It was pointed out (Nature, 1948, 162, 746) that if complexes of the divalent transition metals Mn, Fe, Co, Ni, Cu and Zn were examined, the stabilities rose to a maximum at copper and decreased for zinc in a very regular manner whether the ligand was ammonia, ethylenediamine, propylenediamine or salicylaldehyde (see Figure 2).

FIGURE II



The numbers give the value of n in log k_n for: ◐, ammonia; O, ethylene diammine; X, propylene diammine; ◗, salicylaldehyde.

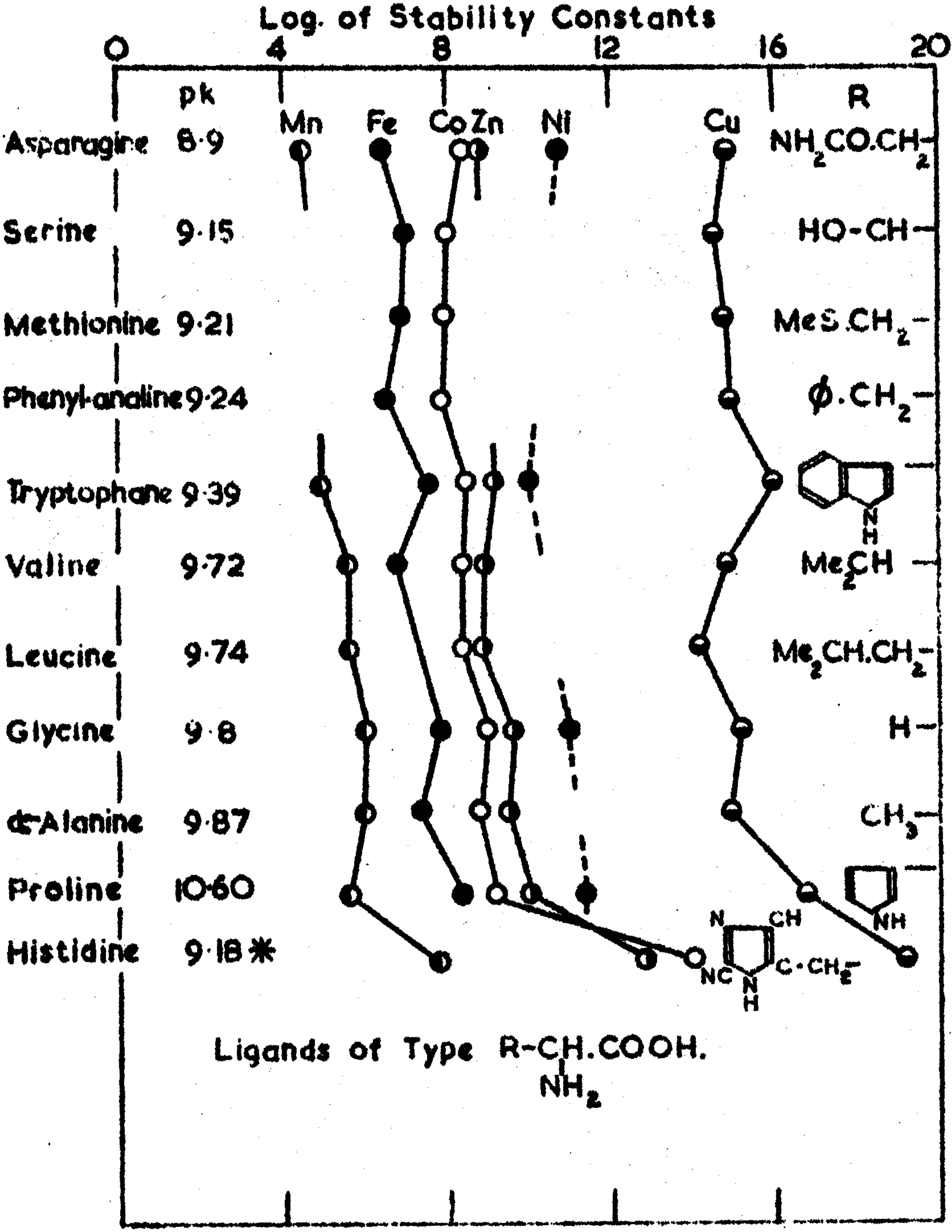
This sequence of stabilities Mn < Fe < Co < Ni < Cu > Zn was also supported by evidence of a more indirect character derived from considerations of the pH of precipitation or extraction of metal complexes with dithizone, oxine or quinaldinic acid (Table VIII).

TABLE VIII

Metal	"Oxine"; pH for 50% precipitation	"Dithizone"; pH for 50% extraction with carbon tetrachloride	Quinaldinic acid; pH for incipient precipitation	Salicylaldehyde; log k_1k_2 in aqueous dioxane
Mn	4.8	~9	-	6.8
Fe	-	5.6	-	7.6
Co	3.2	4.9	3.9	8.3
Ni	3.2	3.0	3.9	9.2
Cu	2.3	1.0	0.5	13.3
Zn	3.1	3.2	1.85	8.1
Pd	-	~-2.0	2.5	14.8
Cd	4.2	4.1	3.2	7.8
Pt	-	~ -2.0	-	-
Hg	-	~ -2.0	0.2	6.8
Pb	5.2	5.5	3.6	9.1

A good deal of quantitative evidence has since appeared which confirms the sequence of increasing stabilities given above. In addition to that quoted in Table IV data on a large number of amino-acid complexes appears in Figure 3. Here the only inversion of order (Co < Zn) appears in the case of histidine which may function as a tridentate group. Some data from Prof. Schwarzenbach is shown in Table VIII. Copper again shows certain peculiarities which derive on the one hand from the fact that it forms only four stable orbitals (so that k_5 for the addition of ammonia and k_3 for ethylene and other diamines) and on the other from the fact that these stable orbitals favour planar co-ordination at points at the corner of a square

FIGURE III


Log. of Stability Constants
0
4
8
12
16
20
pk
Mn
Fe
Co
Zn
Ni
Cu
R
Asparagine 8·9
Serine 9·15
Methionine 9·21
Phenyl-analine 9·24
Tryptophane 9·39
Valine 9·72
Leucine 9·74
Glycine 9·8
dl-Alanine 9·87
Proline 10·60
Histidine 9·18 *
$NH_2CO.CH_2-$
HO-CH-
$MeS.CH_2-$
$\phi.CH_2-$
NH
Me_2CH-
$Me_2CH.CH_2-$
H-
CH_3-
NH
N CH NC N H C·CH_2-
Ligands of Type R-CH.COOH. NH_2

(so that a second molecule of "dien" $NH_2.CH_2.CH_2.NH.CH_2.CH_2.NH_2$ can only be attached through one nitrogen atom). Orbital and stereochemical factors may thus be expected to modify the "natural" order of stabilities. It is, of course, significant that the "natural" order is that of increasing atomic number and runs parallel to the electron affinity of the corresponding ions - as measured by the sum of the first and second ionisation potentials:-

Mn	Fe	Co	Ni	Cu	Zn	
23.1	24.0	25.8	25.8[1]	27.9	27.3	(electron-volts)

An interesting confirmation of the order of stabilities noted here is afforded by work by Pedersen (1949) on the kinetics of decarboxylation of the nitroacetate ion:-

$$NO_2.CH_2.COO^- \longrightarrow {}^-OON:CH_2 + CO_2.$$

This reaction is anti-catalysed by hydrogen ions and by metal ions and by assuming that a 1:1 complex is formed, it was possible to calculate the stability of this complex. The values found for K = [Metal ····NA] /[Metal] [NA] at constant ionic-strength 0.6 are as follows:-

H^+ 21.7	Be^{2+} 1.82					
	Mg^{2+} 0.65	Al^{3+} 3.05				
	Co^{2+} 0.50		Co^{2+} 1.00	Ni^{2+} 1.14	Cu^{2+} 2.77	Zn^{2+} 1.08
	Ba^{2+} 0.					Cd^{2+} 1.54
					Pb^{2+} 1.39	

Mellor and Maley noted independently that the order of stability of certain metal complexes was independent of the ligand involved and quote this as Mg < Mn < Fe < Cd < Zn < Co < Ni < Cu < Pd. But this is not closely born out by later work, for Zn and Co often change places (c.f. the example of histidine above) though we always find Co < Cu > Zn. The inclusion of Mg, Cd and Pd does in fact rather tend to obscure the fundamental connection between electronic structure, ionisation potential and co-ordinating power.

Anomalies arising from Orbital Changes

In every case so far quoted the complexes of ferrous iron have been weaker than those of Co, Ni and Cu in that order. Now red ferrous tris-phenanthroline ions form a well-known analytical test for ferrous ions and their persistence in quite strongly acid solutions is a clear indication of their considerable stability. Kolthoff reports $K_3 = k_1k_2k_3 \sim 10^{21}$. But then we should expect still higher stabilities for the tris-phenanthroline complexes of Co, Ni, Cu and even Zn! These ions should therefore interfere very seriously with the absorptiometric determination of Fe^{++} - which is certainly not the case in practice - and we must infer that for some reason or other they form weaker complexes than those of ferrous iron. Before asking ourselves why this may be, it is significant that the tris-complex of iron and αα'-dipyridyl is also one of high stability with $\log k_3 \sim 17.0$ (25°). Now Krumholtz has recently found $\log k_1 = 4.4$ (25°) whilst Baxendale and George find $\log k_1 = 4.2$ (35°). It follows that $\log k_1k_2$ must be $17.0 - 4.4 = 12.6$; so that even if $k_2 = k_3$ the values of these stability constants ($\log k_2 = \log k_3 = 6.3$) would be <u>greater</u> than the experimentally found value for $\log k_1$. Actually, the kinetic measurements at 35° suggest that $\log k_2 < 5$ so that $\log k_3 > 7$. This remarkable result can only mean that there is a greater free-energy change on co-ordinating the third molecule of dipyridyl than on co-ordinating the second or first and we may confidently predict that similar data will be forthcoming for the complexing of ferrous iron and phenanthroline. Now it is well known that the ferrous iron is paramagnetic in aqueous solution and the paramagnetism of the feeble diamine complexes suggests that these involve iron with the electronic structure (2) (8) (2,6 :....) in which there are four unpaired electrons and no d-orbitals available for bond-formation. If, however, a rearrangement of the electron levels takes place to give ferrous iron with the electronic structure (2) (8) (2,6 :::), the resulting complexes will be diamagnetic and two d-orbitals will be available for the formation of strong octahedral d^2sp^3 orbitals. It is well known that the tris-phenanthroline complexes of ferrous iron are diamagnetic and resolvable into optical enantiomorphs in agreement with this electronic configuration and we may suppose that whilst the first (and possibly the second) dipyridyl or phenanthroline ligand replaces water without profoundedly modifying the structure of the central paramagnetic ferrous ion (being attached by relatively weak "ionic" bonds), the co-ordination of the third ligand is accompanied by a profound electronic rearrangement with electron sharing leading to loss of paramagnetism and the provision of vacant d-orbitals so essential to the formation of a tightly bound complex. Kolthoff has recently reported $\log k_1 = 5.9$ for ferrous iron and o-phenanthroline, with evidence that $\log k_2$ is very small; since $\log K_3 = \log k_1k_2k_3 = 21.5$, it follows that once again $k_1 \sim k_2 < k_3$. If this explanation is correct, we should not expect any similar derangement of the ordinary sequence of stability values viz. $k_1 > k_2 > k_3$ in the case of the complexes of zinc with phenanthroline, for with this ion the electronic structure (2) (8) (2, 6, 10) does not permit of any similar rearrangements. It is thus of special interest that in Mss. received last week from Prof. Kolthoff there was the following (unpublished) data for the o-phenanthroline complexes of zinc: $\log k_1 = 6.43$, $\log k_2 = 5.72$, and $\log k_3 = 4.84$. The regular decrease in affinity for successive ligand molecules follows the "normal" pattern whilst the overall stability $\log K_3 = 17.0$ is less than that for the corresponding Fe complex.

Wherever the nature of the ligand is such as to favour electron-sharing in the ferrous ion, and the consequent liberation of d-orbitals, we may anticipate unusually strong complexes with a consequent inversion of "order". This is illustrated for Cd and Fe in Table IX.

TABLE IX

	4 NH_3	3 En	4 Py	"Trien"	3 dipy	3 phenan
Cd	6.5	12.2	2.5	10.7	10.5	15.2
Fe	~ 2	9.5	< 0	8.8	16.5	21.5
Δ	$\sim +4$	+2.7	$\sim +2$	+1.9	-6.0	-6.3
Stability Cd > Fe					Fe > Cd	

Time does not permit of any detailed discussion of the very interesting complexes of silver ions with amines where commonly $k_1 < k_2$. It may well be that there too orbital rearaangements play an important role, for the experimental result could be explained if the first ligand molecule were attached "ionically" whilst a pair of strong collinear sp orbitals were brought into play when the next ligand becomes co-ordinated.

GENERAL DISCUSSION

Prof. Sidgwick said that the observation that the energy change in the putting on or splitting off of the second molecule of a ligand was less than that for the first, was general. There are very few examples outside of co-ordination chemistry where an atom combines with different numbers of another atom but when it occurs, e.g. PCl_3, PCl_5, the second attachment is nearly always about 80% weaker than the first.

Prof. Albert said that the work which had been described was of exceptional interest to biochemists. Since the publication of Prof. Bjerrum's work in 1941, it has been possible to investigate equilibria between various biologically important metallic ions and vital cell-constituents which combined with them. From the practical point of view it is rather better to make use of the technique of Prof. Bjerrum's pupils, Flood and Loras published in Tidsskr. Kjemi (1944 and 1945) in Norwegian. The calculations are more straightforward and more applicable to actual compounds. The practical limitation is that these compounds should be soluble to the extent of 0.001-M. It has long been known that proteins and porphyrins combine with heavy metals in nature and recently we have shown that pteridines, purines and riboflavine have a high affinity for metallic ions. We have published the relevant stability constants and also those for amino acid complexes where only rough values have been previously available. (However, Mellor and Maley have published some work in this field while our results were in the press (Biochem. J.)).

Prof. Albert queried the term "natural order" used by Dr. Irving. He said it would be better to call it the Mellor and Maley order or the Irving order since it was found that the order of the metals (as regards stability of their complexes) changed when other ligands for example riboflavine or the pteridines were considered. The order is also upset with the purines and the nucleic acids. Nature has, perhaps by trial and error, picked on compounds for use in the body which are rather exceptional when compared with those made in the laboratory. Also with the pteridines this matter of having K_2 smaller than K_1 by a factor of eightfold is disturbed in the case of Cu. The second molecule of 4-hydroxypteridine goes on to Cu almost as readily as the first. On the other hand, with Co the addition is normal and the statistical effect 1:8 for $K_2:K_1$ is obtained.

Dr. P George commented on the results of kinetic and equilibrium measurements on the ferrous ion - dipyridyl reaction carried out in collaboration with J.H. Baxendale (Trans. Far. Soc., 46, 55, 736, 1950).

The red complex ion $Fe(Dipy)_3^{2+}$ was shown to be formed through two intermediates according to the mechanism:

$$\begin{array}{lcl}
Fe^{2+} + Dipy \rightleftharpoons Fe\,Dipy^{2+} & & K_1 \\
Fe\,Dipy^{2+} + Dipy \rightleftharpoons Fe\,(Dipy)_2^{2+} & & K_2 \\
Fe\,(Dipy)_2^{2+} + Dipy \rightleftharpoons Fe\,(Dipy)_3^{2+} & & K_3
\end{array}$$

in which each step is understood to be the replacement of two of the water molecules in the solvation shell of the ferrous ion by a dipyridyl molecule. The overall equilibrium constant $K_1K_2K_3$ was found to be $1.15 \times 10^{17} M.^{-3}$ at 25°C. The constant $K_1 = 1.6 \times 10^4 M.^{-1}$ at 35°C. and whilst K_2 could not be determined exactly, measurements showed that at 35°C. $K_2 < 10^5 M^{-1}$ and hence $K_3 > 2 \times 10^7 M^{-1}$.

The overall heat of formation of $Fe\ (Dipy)_3^{2+}$ is 24.3 ± 1.3 k. cals and the heat of formation of the first intermediate $Fe\ Dipy^{2+}$ is 7.5 ± 2.0 k. cals. Calculation shows that the entropies of formation are within experimental error zero in each case, and it is therefore reasonable to assume that the entropy of formation of $Fe(Dipy)_2^{2+}$ is also about zero. Using this in conjunction with the maximum value of $10^5 M^{-1}$ estimated for K_2 it follows that the heat of formation of $Fe(Dipy)_2^{2+}$ in the second step is probably less than 7 k. cal. Hence the heats evolved on the successive additions of dipyridyl to Fe^{2+} are 7.5 k. cal. for the first, 7 k. cal. for the second and 10 k. cal. for the third.

Bjerrum showed that in the formation of hexammine complexes the addition of successive NH_3 molecules involves about the same heat of reaction which varies from 2 - 3 k. cal. depending on the particular metal ion. The overall entropy change is of the order -20 e.u. The greater stability of $Fe\ (Dipy)_3^{2+}$ thus arises from a higher overall heat of formation of at least 6 k. cals and a greater entropy of formation of about 20 e.u. This larger entropy of formation of the translational entropy for the formation of the complex involves the removal of three dipyridyl molecules from solution and the liberation of six water molecules in contrast to the ammine complex where there is no net increase in the number of free molecules. Entropy considerations thus favour the stability of chelate complexes.

A value of zero for the entropy of formation of $Fe(Dipy)_3^{2+}$ is in satisfactory quantitative agreement with the gain in entropy in liberating the six co-ordinated water molecules in the solvation shell if the three dipyridyl molecules suffer an entropy loss comparable to the entropy of freezing. This is reasonable in view of the rigid structure of the $Fe(Dipy)_3^{2+}$ ion as evidenced by the fact that it can be resolved into optical isomers.

Approximate calculations from thermochemical data show that the Fe - O and Fe - N bond energies in $Fe(H_2O)_6^{2+}$ and $Fe(Dipy)_3^{2+}$ are about 65 and 82 k.cal respectively.

Kinetic studies showed that the formation of $Fe(Dipy)_3^{2+}$ is a fourth order reaction which can be explained if the reaction of $Fe(Dipy)_2^{2+}$ with the last dipyridyl molecule is the rate determining step. The velocity constant is 8.4 ± 1.3 $M.^{-3}$ min^{-1} and is temperature independent. The dissociation is a first order reaction with the rate constant $k_d = 3 \times 10^{17} \exp.(-\frac{26,000}{RT})\ min^{-1}$. It is interesting to observe that this activation energy is of the same magnitude as the overall heat of formation. Since the dissociation reaction involves the replacement of one dipyridyl molecule by two water molecules giving $Fe(Dipy)_2^{2+}$ this large activation energy means that a very considerable expansion in the structure of $Fe(Dipy)_3^{2+}$ is necessary to accommodate the two water molecules in the transition state. A certain amount of disorganisation within the molecule would be expected to accompany this, and it is revealed by the high temperature independent factor of 10^{17}.

Quantitative observations showed that the first intermediate $FeDipy^{2+}$ dissociates extremely rapidly. The central bonds in this molecule are fairly certainly ionic whereas those in $Fe(Dipy)_3^{2+}$ are covalent. This attractive correlation though is fortuitous for the heats of formation per dipyridyl molecule are comparable and the dipyridyl molecule has the same restricted freedom of motion in both complexes.

COMPLEXES OF SOME LIGHTER TRANSITION ELEMENTS WITH A DI(TERTIARY ARSINE)

By Dr. R.S. Nyholm

(University College, London)

Summary of Lecture

1. Introduction

(a) Tertiary arsines such as Et_3As, Ph_3P, Ph_2AsMe etc. are used fairly widely as ligands; Dr. Mann has just discussed complexes of Hg and Cd.

(b) They have properties which make them convenient for certain purposes:

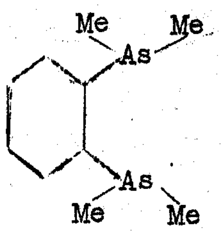
(i) Practically neutral and hence do not precipitate metal hydroxides in presence of water.

(ii) Non-ionic complexes are usually soluble in organic media and hence can do <u>molecular weights</u> and <u>dipole moments</u>, and elucidate stereochemistry. (Cf $PtCl_2.2NH_3$ where one could do neither with reliability).

(iii) Reluctance to give other than covalent bonds.

(c) We have been interested for some years in elements in Group VIII with which tertiary arsine complexes not previously investigated and have studied these to characterise, determine stereochemistry, co-ordination number, bond type etc.

(d) This investigation described complexes of the chelate group, <u>o</u>-phenylenebis(dimethylarsine) i.e.



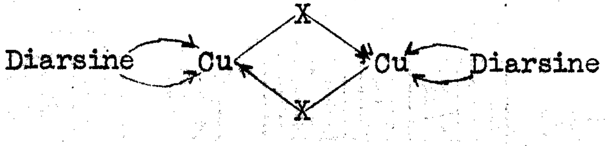
First described by Chatt and Mann (1939) who showed it formed very strong bonds with Pd. Later Allison and Mann described its complexes with Sn(IV). The strength of the bonds suggested that it would form complexes with the more electropositive metals of Group VIII (Fe, Co, Ni) and this study was originally undertaken to try and isolate two types of complex:

(i) NiX_2.diarsine and CoX_2.diarsine, vary X and note any stereochemical change.

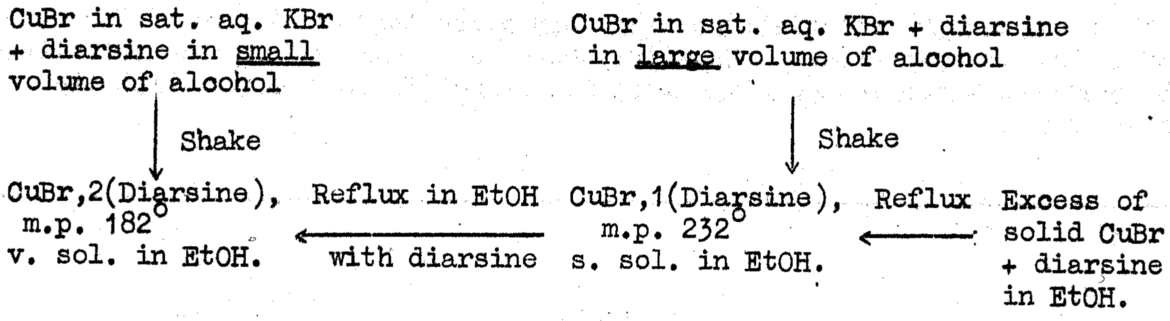
(ii) Bridged complexes of octahedrally co-ordinated elements e.g. ferric iron, tervalent rhodium etc. and to find (possibly) new bridged structures.

2. <u>Complexes formed</u>: (With Fe, Co, Ni and Cu).

<u>Univalent State</u>: Only copper gives complexes in this valency state. Two types are obtained, CuX.1diarsine and CuX.2diarsine. The latter are very soluble in alcohol, react with $AgNO_3$, give a perchlorate of the formula $[Cu(diarsine)_2]ClO_4$ and conduct in nitrobenzene. Hence they are salts $[Cu(diarsine)_2]ClO_4$. The other type were believed at first to be bridged e.g.



However, treatment with $HClO_4$ gives the same perchlorate as before, they conduct in $PhNO_2$, and their molecular weights in $PhNO_2$ and acetone are half the calculated value. Hence the formula $[Cu(diarsine)_2]CuX_2$ is indicated. Furthermore, treatment with py fails to split any supposed bridge.



<u>Bivalent State</u>

<u>Iron</u>: Shaking $FeBr_2$ or FeI_2 with diarsine in $EtOH-H_2O$ gives a yellow precipitate insoluble in all solvents. Diamagnetic and of the formula $[Fe(diarsine)_2X_2]^0$. Obviously an octahedral non-ionic complex. Chloride shows very ready oxidation to a pink colour and in presence of air and $HClO_4$ gives the ferric complex in a few minutes. This is significant (see later).

<u>Cobalt</u>: Co halides in alcohol with the diarsine give compounds of the formula $[Co(diarsine)_2X_2]$. Insoluble, high melting point (decomp.) obviously salt-like and magnetic moment about 2-2.4. Hence a square complex of bivalent cobalt.

<u>Nickel</u>: As with cobalt, but very much more soluble in alcohol and water and deep red in colour. Diamagnetic and hence square.

Calculated magnetic moments for various types of iron complexes

Complex	Electronic arrangement									Calculated magnetic moment (μ).
	3d					4s	4p			
Ferric covalent octahedral (d^2sp^3 bonds)	↓↑	↓↑	↓	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	1.73
Ferric ionic, octahedral or tetrahedral	↓	↓	↓	↓	↓					5.92
Ferric covalent planar (dsp^2 bonds)	↓↑	↓	↓	↓	↓↑	↓↑	↓↑	↓↑		3.88
Ferrous covalent octahedral (d^2sp^3 bonds)	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	0.00
Ferrous ionic, octahedral or tetrahedral	↓↑	↓	↓	↓	↓					4.90
Ferrous covalent planar (dsp^2 bonds)	↓↑	↓↑	↓	↓	↓↑	↓↑	↓↑	↓↑		2.83

These values are calculated on the assumption that the whole of the moment is due to spin alone. Usually, there is a small orbital contribution which increases these values slightly; its effect is most marked with the lower values.

Calculated magnetic moments for cobalt complexes

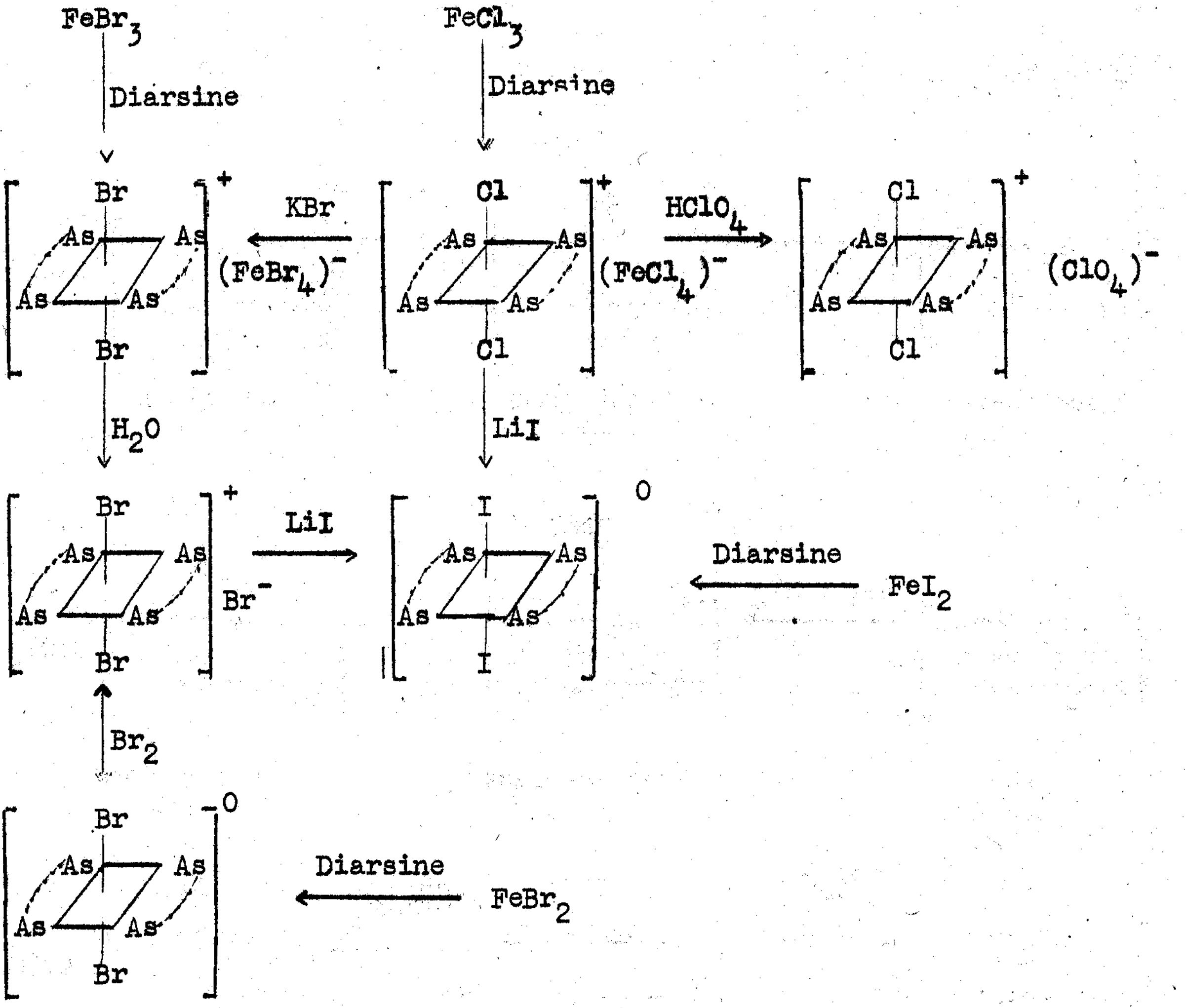
Complex	Electronic arrangement										Calculated magnetic moment (B.M.).
	3d					4s	4p			4d(?)	
(i) Cobaltous (ionic) (tetrahedral or octahedral)	↓↑	↓↑	↓	↓	↓						3.88
(ii) Cobaltous (tetrahedral) (sp^3 bonds)	↓↑	↓↑	↓	↓	↓	↓↑	↓↑	↓↑	↓↑		3.88
(iii) Cobaltous, planar (dsp^2 bonds).	↓↑	↓↑	↓↑	↓	↓↑	↓↑	↓↑	↓↑			1.73
(iv) Cobaltous, octahedral (d^2sp^3 bonds)	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓	1.73
(v) Cobaltic (ionic)	↓↑	↓	↓	↓	↓						4.90
(vi) Cobaltic, octahedral (d^2sp^3 bonds)	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑		0.0

Calculated magnetic moments for nickel complexes

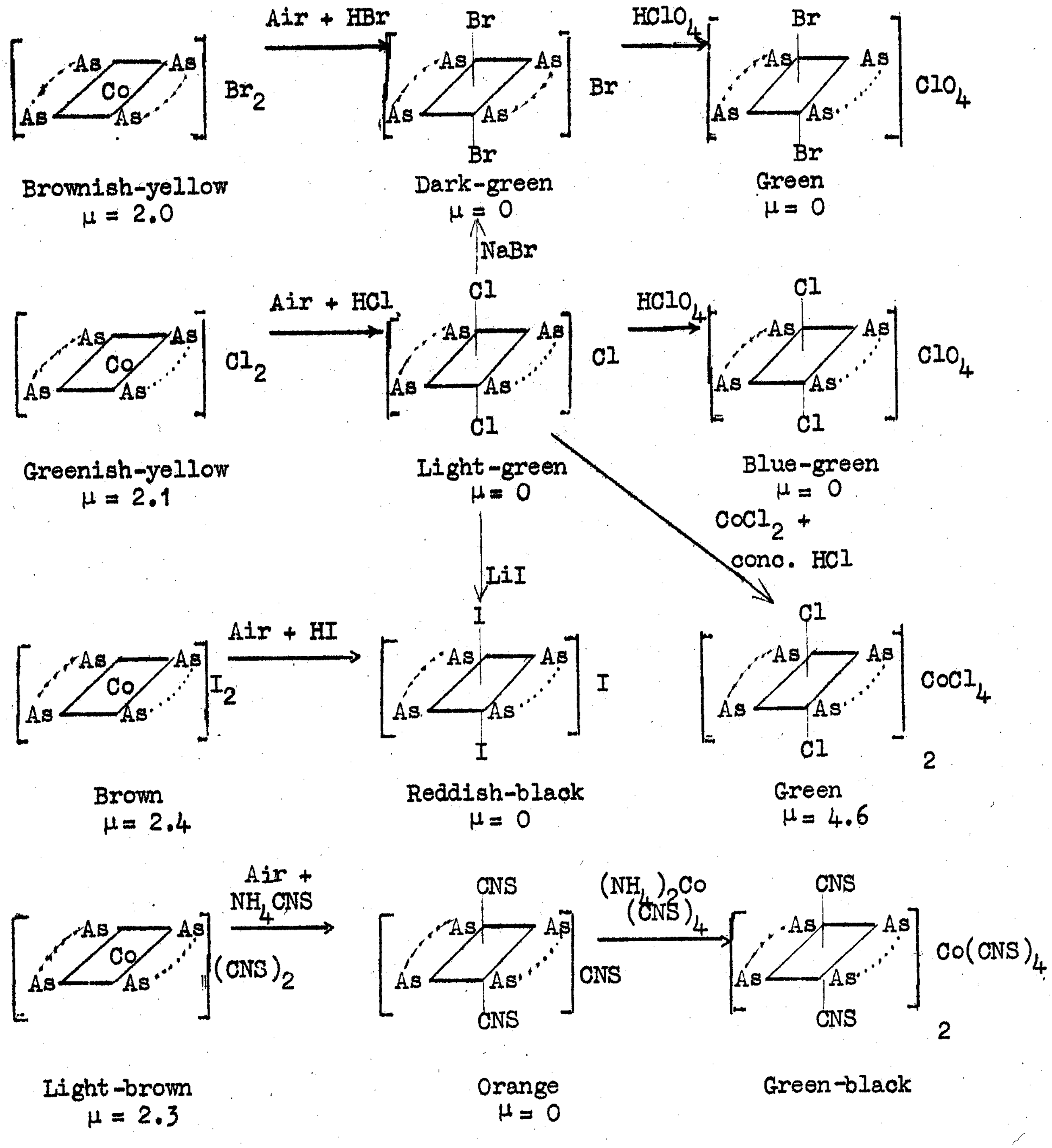
Complex	Electronic arrangement 3d	4s	4p	4d(?)	Calculated magnetic moment (B.M.).
(i) Nickelous covalent planar (dsp^2 bonds)	[↓↑] [↓↑] [↓↑] [↓↑] [↓↑]	[↓↑]	[↓↑] [↓↑] [ ]		0.0
(ii) Nickelous ionic, octahedral or tetrahedral	[↓↑] [↓↑] [↓↑] [↓] [↓]	[ ]	[ ] [ ] [ ]		2.83
(iii) Nickelous covalent tetrahedral (sp^3 bonds)	[↓↑] [↓↑] [↓↑] [↓] [↓]	[↓↑]	[↓↑] [↓↑] [↓↑]		2.83
(iv) Nickelous covalent octahedral (d^{2}sp^3 bonds)	[↓↑] [↓↑] [↓↑] [↓↑] [↓↑]	[↓↑]	[↓↑] [↓↑] [↓↑]	[↓] [↓]	2.83
(v) Nickelic covalent planar (dsp^2 bonds)	[↓↑] [↓↑] [↓↑] [↓] [↓↑]	[↓↑]	[↓↑] [↓↑] [ ]		1.73
(vi) Nickelic covalent octahedral (d^{2}sp^3 bonds)	[↓↑] [↓↑] [↓↑] [↓↑] [↓↑]	[↓↑]	[↓↑] [↓↑] [↓↑]	[↓]	1.73
(vii) Nickelic covalent square pyramid (dsp^3 bonds)	[↓↑] [↓↑] [↓↑] [↓] [↓↑]	[↓↑]	[↓↑] [↓↑] [↓↑]		1.73

Tervalent State

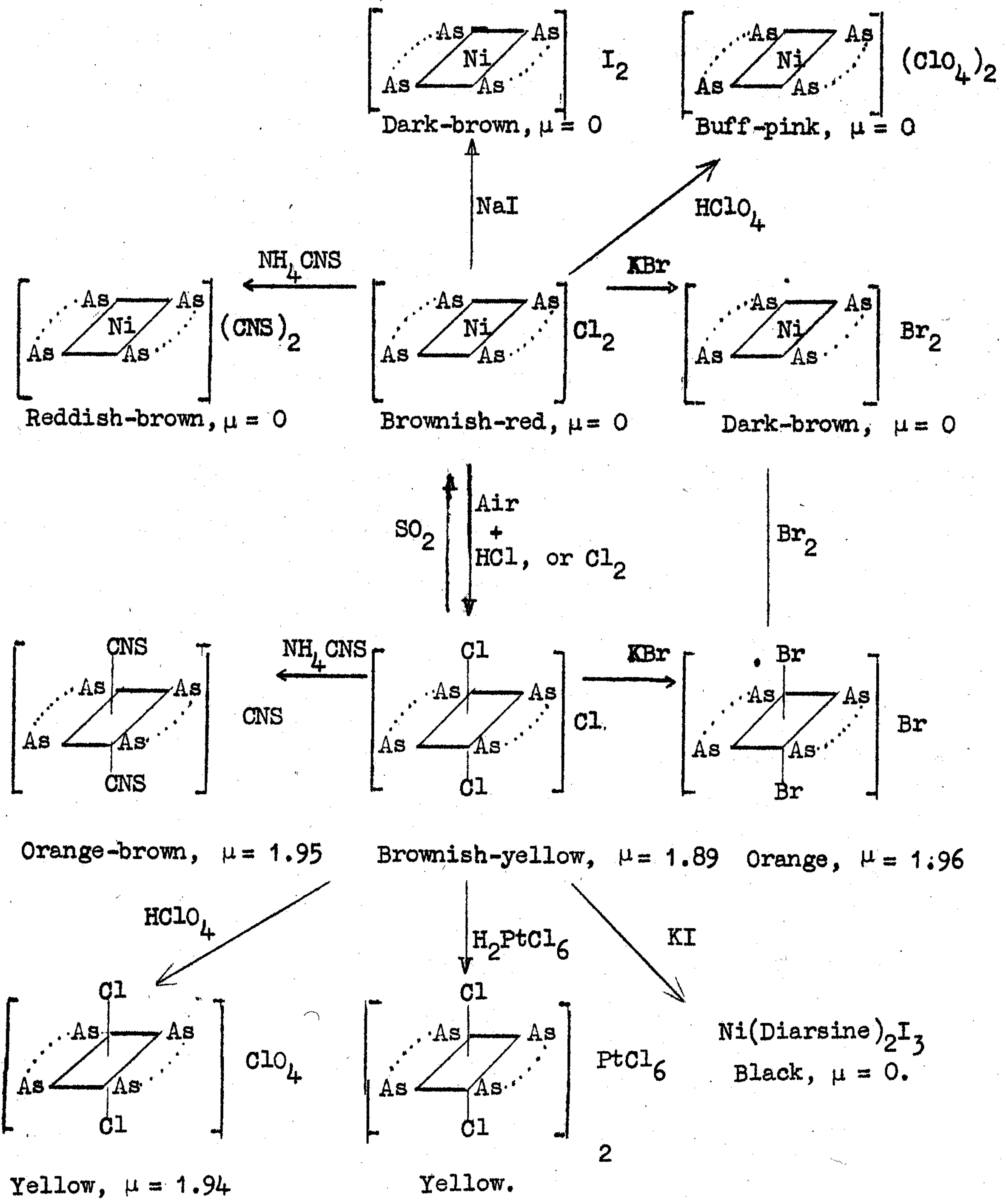
Iron: $FeCl_3$ or $FeBr_3$ with diarsine in EtOH or benzene gives red or chocolate brown precipitate with diarsine. These dissolve in acetone or $PhNO_2$ and give perchlorates with $HClO_4$ of the formula $[FeX_2(diarsine)_2]ClO_4$ for which u = 2.3, i.e. covalent octahedral bonds. Other compounds are not bridged but have the formula $[FeX_2(diarsine)_2][FeX_4]$ with μ = about 4.6 B.M. The diagram below shows relationship between ferrous and ferric complexes:



Cobalt: Aerial oxidation of the bivalent salts give tervalent octahedral complexes readily. With chloride, one can get a compound $[CoCl_2(\text{diarsine})_2]_2[CoCl_4]$ confirmed by perchlorate and magnetic moments. Also bromide and iodide. Solubility of Co(II) compound affects speed of oxidation. Comment on extraordinary ease of formation of the cobaltic thiocyanate.



Nickel: Attempts to isolate $NiCl_2$.diarsine by refluxing $Ni(diarsine)_2Cl_2$ with $NiCl_2$ in EtOH in air gives $NiCl_3.(diarsine)_2$. This compound is soluble in water and has molecular conductivity = 120 reciprocal ohms. It gives a perchlorate and platinichloride of the formula $[NiCl_2A_2]X$ and all are paramagnetic with μ = 1.9 B.M. Definitely oxidation; hence is oxidation of Ni or As. Magnetic moments supports Ni(III)



On the following page the behaviour of di- and tervalent iron cobalt, and nickel is compared with regards to complex formation with o-phenylenebisdimethylarsine:

Complex salts formed by iron, cobalt, and nickel with a di(tertiary arsine)

Iron

Bivalent $[FeA_2X_2]^0$.

X = Br, I, CNS; non-electrolytes, diamagnetic, μ = 0, covalent d^2sp^3 bonds.

Octahedral (six-covalent).

Tervalent

$[FeX_2A_2][FeX_4]$.

X = Cl, Br; paramagnetic, = 2.3 for cation and μ = 5.9 for anion.

$[FeBr_2A_2]X$.

X = Br, ClO_4, cation covalent, d^2sp^3 bonds.

Octahedral

Cobalt

Bivalent $[CoA_2]X_2$.

X = Cl, Br, I, CNS; salts, paramagnetic, μ = 2.0-2.4, covalent dsp^2 bonds.

Planar (four-covalent).

Tervalent

$[CoX_2A_2]_2[CoX_4]$.

X = Cl, CNS; paramagnetic, μ = 0 for cation and μ = 4.4 for anion.

$[CoX_2A_2]X$.

X = Cl, Br, I, CNS, cation contains covalent d^2sp^3 bonds.

Octahedral

Nickel

Bivalent $[NiA_2]X_2$.

X = Cl, Br, I, CNS, ClO_4; salts, diamagnetic, μ = 0, covalent dsp^2 bonds.

Planar (four-covalent)

$[NiA_3](ClO_4)_2$; diamagnetic, μ = 0.

Octahedral

Tervalent

$[NiX_2A_2]X$.

X = Cl, Br, CNS; paramagnetic, μ = 1.9.

$[NiCl_2A_2]B$.

B = ClO_4, $\frac{1}{2}PtCl_6$, μ = 1.9, orbitals doubtful.

Octahedral

CONCLUSIONS:

1. Co-ordination Numbers

Nothing unusual. Univalent copper presumably tetrahedral; bivalent iron octahedral and bivalent cobalt and nickel are square. All tervalent elements are octahedral.

2. Bond Type

As judged from magnetic moments all are covalent.

3. Stability

Very high, thus with Fe(III) apart from ferricyanide and dipyridyl and o-phenanthroline complexes, no other covalent bonds of ferric iron are known. Cobalt really remarkable, forming even a stable tervalent iodide with two iodine atoms and two As atoms therein. Nickel most remarkable of all in that one gets Ni(III) complexes.

4. Number of Chelate Groups Attached

Always tend to get two only, except with Ni(II) in which the compound $[Ni(diarsine)_3][ClO_4]_2$ is described.

5. Failure to obtain bridged octahedral complexes and bridged Cu complexes.

6. Failure to obtain compounds such as $[NiCl_2(diarsine)]^0$. There seems definite tendency to get two chelates attached.

7. Stabilisation

Although Fe, Co and Ni stabilised in their higher valency states by this chelate group, Cu stabilised in univalent state. Implication is not yet clear but whereas to get a square complex of bivalent Ni and Co, it is necessary to use least electronegative ligands, one can use the most electronegative with Cu e.g. water and NH_3. Ethylenediamine with Fe, Co, Ni gives ion-dipole bonds and no covalent complexes, yet with this ditertiary arsine all give covalent bonds. Ditertiary arsine stabilises covalent bonded state Fe(II) → Fe(III) etc. Failure to stabilise Cu(II) of. Cu(I) indicates something anomalous with Cu(II).

PROBLEMS ARISING FROM THE WORK

1. Stereochemistry of Co(III) complexes - cis or trans. X-ray or attempt to resolve, is only answer.
2. Diamagnetism of $[Ni(diarsine)_3][ClO_4]_2$. This is difficult to explain.
3. Diarsine + NiI_2 ⟶ in alcohol ⟶ brown square diamagnetic $[NiA_2]I_2$.

   Diarsine + NiI_2 ⟶ in water ⟶ green diamagnetic $[NiA_2I_2]^o$, octahedral?
4. Comparison with $MeSCH_2CH_2SMe$ (Foss) and corresponding aromatic one. Also comparison with $Me_2AsCH_2CH_2AsMe_2$.

GENERAL DISCUSSION

Dr. Mann congratulated Nyholm on the work and its presentation. Nyholm had said that tertiary phosphines and arsines were neutral ligands but in fact the phosphines were more basic than the corresponding ammines. Basicity increases from amines to phosphines and then decreases to arsines.

Dr. Palmer said that nickel nitrite formed with ammonia a green paramagnetic complex $Ni(NO_2)_2.4NH_3$. The analogous pyridine complex is red and diamagnetic. This may be an analogous case to the compounds (NiI_2.2 diarsine) mentioned by Dr. Nyholm.

Nyholm said that there were some complex nickel nitrites which were red. Their magnetism appears not to have been studied and it would be interesting to know the nature of the $Ni-NO_2$ bond.

Dr. Anderson stated that from the mechanism of the formation of carbonyls suggested by Hieber other tervalent nickel complexes are known. He asked whether Nyholm had obtained any evidence of Ni(IV) complexes.

Dr. Nyholm replied that he had evidence for the quadrivalent state of nickel from chlorine oxidation of the tervalent complex. One apparent weakness of Pauling's theory of the promotion of electrons has been the fact that $Ni(dipy)_3Cl_2$ cannot be oxidised to a tervalent nickel complex although it would appear that there are two electrons promoted. The answer to the problem is apparently either (a) that in $Ni(dipy)_3Cl_2$ two electrons are not promoted or (b) that a divalent nickel complex can be oxidised if strong covalent bonds (e.g. with the diarsine) are present.

Prof. Sidgwick asked whether it can be proved that diamagnetism was always associated with a planar configuration of nickel and paramagnetism with a tetrahedral.

Dr. Nyholm replied that X-ray studies had been made on diamagnetic complexes and these were all planar but he was not aware of any complete structure determinations of a paramagnetic compound which had been carried out.

Dr. Palmer stated that recently the green paramagnetic compound $Ni(NH_3)_4Cl_2$ had been shown by X-ray studies to be tetrahedral.

Dr. Irving asked whether it would be possible to achieve square bonds (dsp^2) by promoting one of the 3d unpaired electrons of nickel to the 4d shell and then having dsp^2 bonds simultaneously with two unpaired electrons.

Dr. Craig replied that by the principal of maximum multiplicity it is likely that a promotion from the 3d shell would leave three unpaired electrons in that shell instead of one as Irving's idea involved. The whole complex would then have four electrons in singly occupied orbitals instead of two.

Dr. Nyholm finally stated that if you consider Ni(II) and Co(II) one gets square complexes only with the least electronegative groups. In the case of Cu(II) distribution is always planar. Something very fundamental happened in going from Ni and Co to Cu.

THE CO-ORDINATION OF OLEFINS TO PLATINOUS SALTS

By Dr. J. Chatt

(Butterwick Research Laboratories)

Introduction

I have chosen this rather speculative subject because the co-ordination of olefins has received no explanation on the basis of the lone pair theory of co-ordination; it is, in fact, a challenge to that theory.

Few olefin complexes are known and only the platinous series is sufficiently stable for detailed chemical investigation. Typical types are shown in Fig. 1.

TYPES OF ETHYLENE COMPLEXES WITH PLATINOUS CHLORIDE

$K^+[C_2H_4PtCl_3]^-$ 1827

trans-$[C_2H_4,NH_3,PtCl_2]$ 1827

$[(C_2H_4)_2Pt_2Cl_4]$ 1934

cis-$[C_2H_4,NH_3,PtCl_2]$ 1939

$[C_2H_4,NH_3py,PtCl]^+Cl^-$ 1946

$[(C_2H_4)_2PtCl_2]$ [decomposes -10°C at 760 mm. C_2H_4] 1950

Fig. 1

Except that cis- and trans-ethylene-monoammines are about equally stable, their order of decreasing stability is the order of their discovery.

There is ample evidence that these are co-ordination compounds resembling more than any others the carbonyl complexes but differing in some respects from the ammines.

Structures

About eight structures for olefin complexes have been suggested, and these are classified as follows:-

Firstly, those with the character of a platinous alkyl (e.g. Fig. 2).

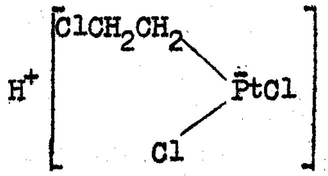


Fig. 2

(Drew, Pinkard, Wardlaw & Cox, J. Chem. Soc., 1932, 997). These may be dismissed because platinous alkyls are unstable, and also the olefin is readily replaced by other olefines as well as CO, pyridine and such. Alkyls do not behave in this manner. Also, ketones are not obtained by reaction with acid chlorides, nor chlorohydrocarbons by reaction with water.

Next, we have those which attempt to make the olefin fit the lone pair theory by using the π electrons in some manner for donation to the metal (e.g. Fig. 3).

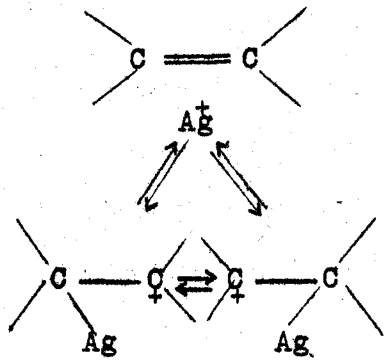


Fig. 3

(Winstein & Lucas, J. Amer. Chem. Soc., 60, 836 (1938)).

If this mechanism operates we should expect some interaction between ethylene and the acceptor alkyls of group 3 elements. We have examined the system ethylene-trimethylborine by taking a freezing point curve of these substances (Fig. 4).

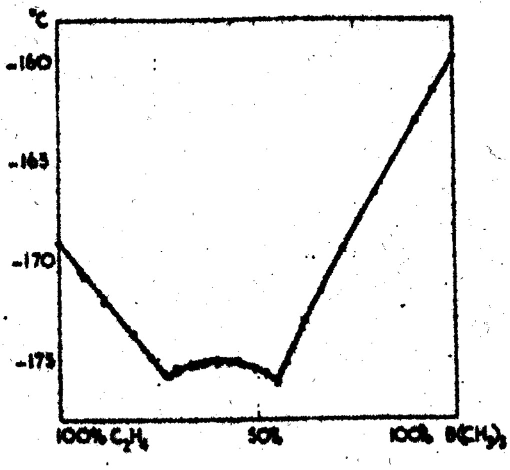


Fig. 4

No one-to-one compound is formed, and a log-mol fraction - $\frac{1}{T}$ plot is a straight line showing that there is no interaction whatsoever between these substances (Fig. 5). This is surprising, as the ionisation potential of the π electrons (10.45V) is slightly less than that of the ammonia lone pair (10.8V) and trimethylborine forms a very stable ammine.

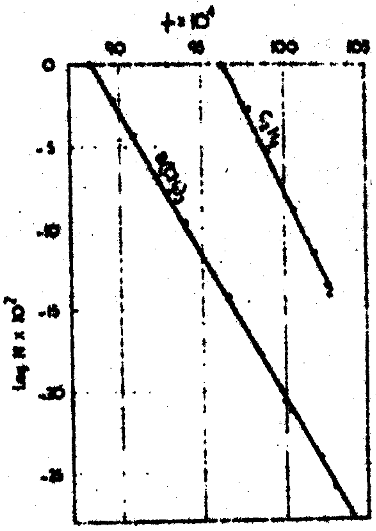


Fig. 5

Finally, we have a vague structure of Hel'man's. She suggests that the π electrons are donated from one carbon atom to the platinum atom whilst the platinum atom donates the two electrons, used in raising its valency from 2 to 4, to the second carbon atom.

The behaviour of ethylene with trimethylborine is clear evidence that something other than simple donation of electrons is involved in olefin co-ordination, and Hel'man's suggestion that d electrons are involved would explain both; why ethylene does not show any interaction with trimethylborine, and also why platinum, which has available d electrons on a similar energy level to s and p should also form the most stable olefine complexes.

Trans influence and similarity to CO.

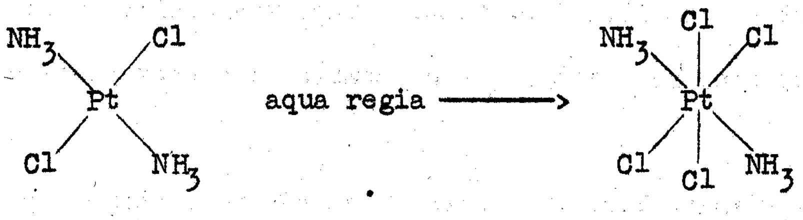
As a second approach to the problem, we asked ourselves - Do the properties of olefin complexes suggest that they are exceptions to co-ordination theory? The answer appears to be, No. They are merely an extreme type, closely similar to CO complexes, rather different from ammines.

A general consideration of the properties of platinous complexes indicate that ligands may be placed in a series of gradually changing character. At one end of the series we have the ethers and amines, at the other carbon monoxide and ethylene, e.g.,

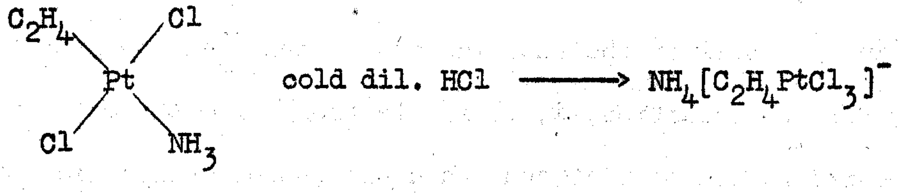
$$Me_2O,\ Me_3N,\ MeNH_2,\ Me_3P,\ Me_2S,\ (NH_2)_2CS,\ CO,\ C_2H_4.$$

Those at the beginning of the series co-ordinate to boron but not to platinous chloride. Those in the centre co-ordinate strongly to platinum but weakly to boron. Those at the end moderately strongly to platinum, slightly or not at all to boron.

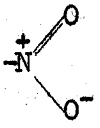
A most significant property of ligands is that named "trans influence" by Chernyaev who discovered it. It is a property of ligands whereby any group in the trans position to themselves in platinous complexes is rendered labile by their presence. It may be illustrated by considering the platinous ammines and trans- $C_2H_4.NH_3.PtCl_2$.



In this reaction the ammonia is not removed even by strong acid but it is immediately removed from ethylene-ammino-dichloroplatinum by dilute hydrochloric acid.



The effect was first noticed for unsaturated ligands, e.g.



, $-CN^-$, $(NH_2)_2C{=}S$, CO, C_2H_4

and appeared to indicate that ethylene retained its double bond after co-ordination.

It was next recognised for dialkyl sulphides and, to a lesser extent, for tertiary phosphines. The effect is thus not due to a double bond, but in neutral ligands appears to be associated with donor atoms capable of raising their covalencies by two units, e.g.,

C_2H_4	$C_2H_4Cl_2$	$C_2H_4{=}O$
CO	$COCl_2$	OC=O
R_3P	R_3PCl_2	$R_3P{=}O$

but not R_3N or R_2O.

Thus ligands showing trans influence are those capable of receiving as well as donating electrons, which is further evidence that perhaps receiving electrons from the metal atom is an important part of their co-ordination.

Evidence from PF_3 complexes

To test this idea, let us consider the phosphines which show trans influence only to a minor extent. R_3P co-ordinates strongly both to boron and platinum. If the R's are replaced by fluorine we would expect the lone pairs to become very inert due to the strong inductive effect of the fluorine atoms. This was confirmed by attempting to combine PF_3 with BF_3 - no combination took place down to -80°C.

If the co-ordinate link is a sort of double bond formed by donation of electrons from the phosphorus and receiving of electrons from the platinum, then this latter effect would be enhanced by the pull of the fluorine atoms, and the electron drift from the metal to phosphorus by neutralising the pull of the fluorine atoms would tend to free the lone pair for co-ordination, i.e., if electrons from the metal take part in co-ordination to platinum, then phosphorus trifluoride should combine strongly with platinum. When we tried this experiment by passing PF_3 over $PtCl_2$ at 250°C., two very stable volatile complexes distilled into the cold parts of the tube $(PF_3)_2PtCl_2$ and $(PF_3PtCl_2)_2$. The latter is so stable it can be distilled without any decomposition at 15 mm. pressure. These compounds resemble the carbonyl platinous halides, which were hitherto the most volatile platinous complexes known; so close is the resemblance that there can be little doubt that the mode of combination of PF_3 and of CO is closely similar.

Further, we have attempted to replace the CO of nickel carbonyl by PF_3 and obtained a mixture boiling over a long range 45-64°C. ($Ni(CO)_4$ = 43°C.), and the top fraction analysed as $Ni(CO)_{1.5}(PF_3)_{2.5}$. We have isolated no pure substance from this mixture as yet, but it seems significant that PF_3 which does not combine with BF_3 can at least partially replace CO from nickel carbonyl, to give a substance of similar character to $Ni(CO)_4$.

Pauling has already suggested that d orbitals of the metal take part in carbonyl formation, giving a type of double bond $Ni{=}C{=}O$. This double bond differs from the familiar double bond of organic chemistry in that the electrons for the σ bond may be considered as supplied by the carbon atom and for the π bond by the nickel. Such a bond may be called a dative double bond as being composed of a dative covalency and a dative π bond together.

<u>Trans</u> influence - associated with a dative double bond.

It seems probable that <u>trans</u>-influence is associated with the existence of a dative double bond, and as ethylene has a very high <u>trans</u> influence, the dative double bond is essential for its co-ordination as it is for the strong co-ordination of CO and PF_3.

For the formation of a dative double bond two conditions are essential:

(1) The metal atom must have available electrons from a filled d orbital.

(2) The donor atom must have a vacant orbital to receive them as well as a lone pair.

This is shown pictorially for CO-Pt in Fig. 6.

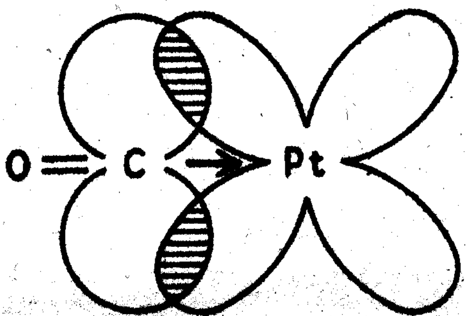
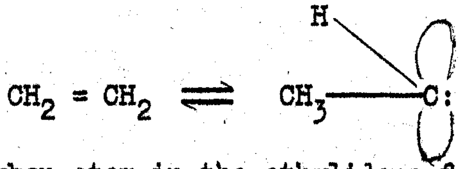


Fig. 6

The co-ordination of olefins.

Now, let us try to apply this to the co-ordination of olefins. Previous attempts to explain co-ordination have been based on a lone pair only. To fit ethylene into the above scheme, it must be given both a lone pair and a vacant orbital. This can be done if ethylene rearranges during co-ordination to give an ethylidene complex.



The divalent carbon atom in the ethylidene form of the molecule has both a lone pair and a vacant orbital. In the complex the lone pair would be donated to platinum and the vacant orbital saturated by overlap with a filled d orbital (Fig. 7). It is exactly analogous to the carbonyl complexes.

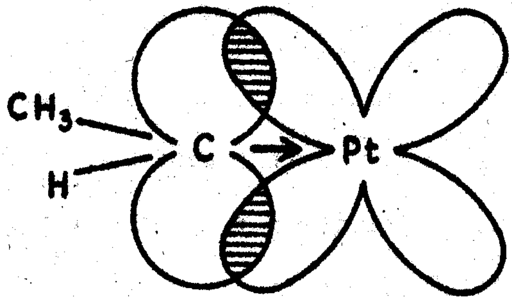


Fig. 7

Explanation of reactions

This structure explains the known reactions of the olefin complexes better than any other.

(1) Displacement reactions

(i) The main reactions are displacement reactions (e.g. the olefin is liberated by reaction with pyridine) and these are simply the reversal of co-ordination so that the liberated ethylidene rearranges to give the original olefin.

(ii) Molecules of only slight trans influence liberate ethylene from the trans position. As the π bond is essential for olefine co-ordination any tendency for a second ligand to draw away electrons from it in formation of its own π bond would weaken the attachment of ethylene. Quite strong co-ordinating groups such as, $p.CH_3C_6H_4NH_2$ with no <u>trans</u> influence, do not replace ethylene.

(2) Reaction with water

The reaction with water is one of the most significant and led Anderson in 1934 to suggest that the attachment of the olefin was by one carbon atom only. He found no evidence of symmetrically substituted ethanes in the reaction products. The reaction is:

$$[CH_3CH{:}PtCl_3]^- + H_2O = CH_3CHO + Pt + 2HCl + Cl^-.$$

It is exactly analogous to the corresponding reaction in the carbonyl series

$$[COPtCl_3]^- + H_2O = CO_2 + Pt + 2HCl + Cl^-$$

(3) Relative stabilities of olefin complexes.

Substitution in the ethylene molecule markedly weakens its tendency to co-ordinate except in two very significant instances. We should expect that the more stable the ethylidene, relative to ethylene form of the olefin, the more readily the olefin will co-ordinate. The stability of the ethylidene will be enhanced if the hydrogen atom attached to the divalent carbon atom is replaced by an aromatic or unsaturated system which after co-ordination would be conjugated to the C=Pt bond. In agreement with this the only two simple olefins $RCH{=}CH_2$ of corresponding co-ordinating power to ethylene are styrene ($R = C_6H_5-$) and butadiene ($R = CH_2{=}CH-$), which does not chelate, all the others are much weaker. If only simple donation of electrons was involved we should have expected propylene to be a stronger donor than styrene, not the reverse as is in fact found. Similarly the indene complex is more stable than the cyclohexene complex.

(4) Effect of ionic charge

Of the platinous complexes $[APtCl_3]^-$, $[ABPtCl_2]^0$ and $[ABCPtCl]^+$ the neutral complex is usually much more stable than the charged complexes, but when $A = C_2H_4$ and $B = NH_3$ the negative and neutral complexes have about equal stability and if $A = B = C_2H_4$ the neutral complex decomposes in an ethylene atmosphere at -10°C., whereas the salt $K[C_2H_4PtCl_3]^-$ is sufficiently stable to be recrystallised, with care, from very dilute hydrochloric acid. Only one example of a positive complex is known and it is very unstable, $A = C_2H_4$, $B = NH_3$, $C = C_5H_5N$.

The carbonyl complexes although they are more stable thermally, presumably because CO is itself a stable molecule, show the same trends in stability. This abnormal order of stability finds an explanation in that we should expect increasing positive charge on the complex to draw in towards the platinum atom the d electrons from the C—Pt π bond, thus increasing the unsaturation of the donor carbon atom and decreasing the stability of the complex.

CIS - TRANS EQUILIBRIA IN THE PLATINOUS SERIES OF COMPOUNDS

By Dr. R.G. Wilkins

(Butterwick Research Laboratories)

This work was undertaken because the results obtained would throw light on the nature of the bond between the ligand and the metal and also give further evidence whether the d-electrons of the platinum take part in this binding. First, it is intended to discuss the methods by which the equilibria were measured and the results obtained. Then how it is related to the general problem of co-ordination.

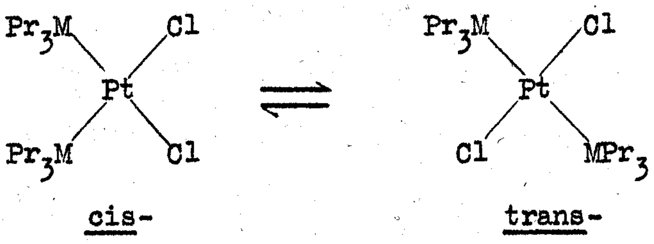
Under suitable conditions all the cis compounds with the formula $(Pr_3M)_2PtCl_2$, where M = P, As, and Sb, isomerise in benzene solution at room temperature to an equilibrium mixture containing a large amount of the corresponding trans compound. In the absence of a catalyst the cis phosphine compound $(Pr_3P)_2PtCl_2$ shows no tendency to isomerise in benzene solution at ordinary temperatures but on the addition of a trace of the free phosphine (Pr_3P) isomerisation is rapid. The pure arsenic compound $(Pr_3As)_2PtCl_2$ isomerises very slowly in the absence of a catalyst while the pure antimony compound $(Pr_3Sb)_2PtCl_2$ isomerises rather more quickly.

The rate of isomerisation and position of equilibrium was measured using the different dielectric properties of the cis- and trans- compounds. When the cis-compound was dissolved in pure benzene, the dielectric constant of the benzene was increased appreciably, while the addition of the trans compound had a very small effect. A subsidiary experiment showed that for low concentrations the dielectric constant of the solution of the cis- compound in benzene was proportional to the weight of cis-compound and consequently by measuring the rate of change of the dielectric constant of the cis-compound in solution, it was possible to obtain the kinetics of the cis - trans change. Measurement of the dielectric constant in solution of (a) the cis-compound (b) the trans-compound and (c) the final equilibrium mixture gave the equilibrium constant (K_E) for the change.

The following (preliminary) results were obtained for the P, As and Sb compounds: (Table I).

TABLE I

Isomerisation results at 25°C. in benzene solution for the reaction:



Compound	Percentage cis- in Equilibrium Mixture	$\frac{[trans]}{[cis]} \equiv K_E$	$-\Delta F$ cals.
M = P	3.2	30	2010
M = As	1.8	55	2370
M = Sb	22.2	3.5	740

It can be seen that under the same conditions, that is in benzene solution where lattice forces do not operate, the cis-Sb compound is the most stable (relative to the trans), while the cis-As compound is the least stable. This is a different result from that which would be expected if the link between the ligand and metal was solely the classical co-ordinate link since, then, the four bonds from the platinum being all similar, the position of the cis-trans equilibria would be determined solely by the repulsion of the larger groups Pr_3M. In this case the relative stabilities of the cis - to trans- isomers would be expected to decrease as M increased in size from P to Sb and the cis-Sb compound would be relatively the least stable.

On the other hand if the ligand is bound by the dative double bond (as outlined by Dr. Chatt previous paper; Nature 165, 637 (1950)), we expect the stability of the cis-compound (relative to the trans) to increase from phosphorus to antimony. For the formation of a dative double bond the ligand must have, in addition to a lone pair, a vacant orbital. If we consider phosphorus the only vacant orbitals are d-orbitals, so we have assumed that there are the orbitals involved in the formation of the dative π-bond. In the case of the trans complex we thus have a qualitative picture something like that shown in Fig. 1.

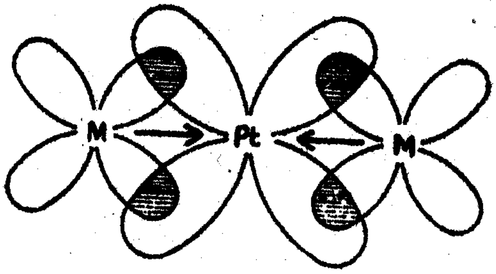


Fig. 1

Now it can be seen that the same orbital is shared in binding the two phosphorus atoms. When we consider the cis-compound, however, there is a d-orbital at right angles to the one shown on the slide so that each phosphorus atom is bound by a different d-orbital. Thus, as the contribution of the d-orbital binding becomes greater, we should expect the cis-complex to become more stable (relative to the trans). Again looking at the orbital diagram, it appears obvious that as the two atoms taking part in this type of binding become more equal in size the overlapping of the d-orbitals should become greater and the π-bonding thus more important. In the series phosphorus, arsenic and antimony the radii are 1.10, 1.18 and 1.36A respectively, and that of platinum is 1.31A. Thus we see that the antimony atom is most close in size to that of the platinum atom. Thus we should expect the greatest π-bonding in the case of the antimony atom and hence the cis-antimony compound (relative to its trans isomer) should be most stable and this is exactly what we have found.

A substantial amount of evidence has been obtained for the following mechanism for the cis - trans isomerisation, illustrated in the case of the antimony compound. (Fig. 2).

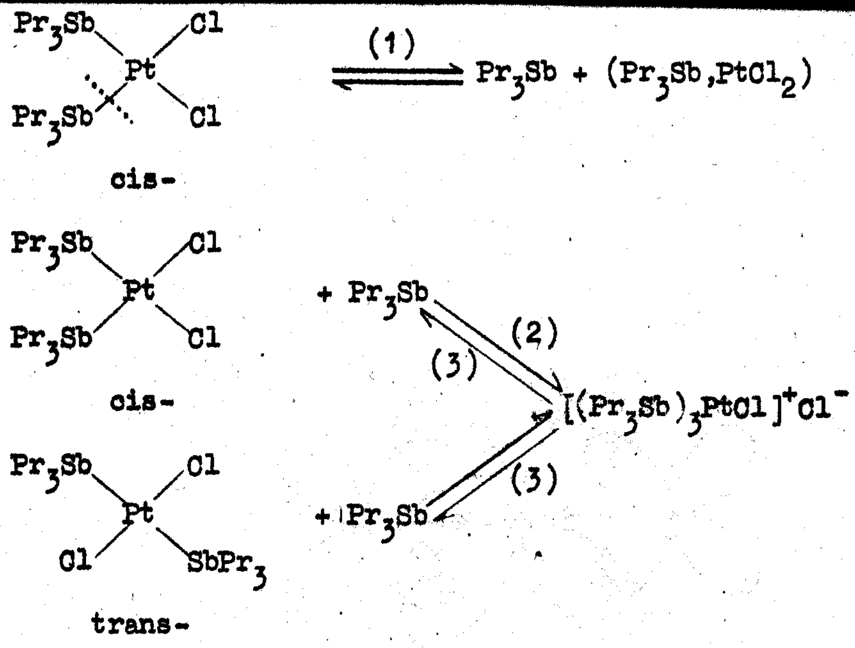


Fig. 2

In stage (1) the cis-compound dissociates reversibly to the two fragments shown: (a) the 3-covalent platinum complex (probably with a transitory existence) and (b) tripropyl stibine. The latter then attaches itself to the original cis-compound and forms the salt (stage (2)) which can then dissociate to give either the original cis-compound or the trans-compound and reliberate tripropyl stibine. Evidence for this mechanism is forthcoming from three points:-

(1) It is known from work by R.S. Nyholm (J.C.S., (1950), 848) that the salt $[(R_3As)_3PtBr]Br$, which is of the type produced by this mechanism, is extremely unstable in benzene solution and decomposes to the bisarsine compound and free arsine.

$$[(R_3As)_3PtBr]Br \longrightarrow [(R_3As)_2PtBr_2]^0 + R_3As$$

(2) The form of rate curves obtained for the isomerisation of the arsenic compound suggested that autocatalysis was taking place (Fig. 3).

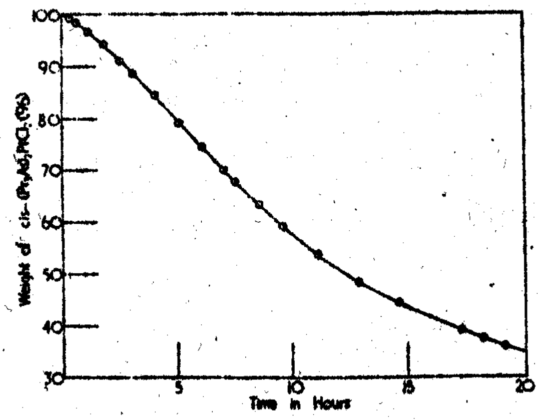


Fig. 3

If the mechanism is correct, an obvious autocatalyst would be Pr_3As which in the case of the analogous phosphine compound would be Pr_3P. In fact as mentioned previously a solution of pure cis - $(Pr_3P)_2PtCl_2$ in benzene shows no tendency to isomerise at 25°C. and stage (1) does not occur appreciably (it is known that the Pt - P link is a strong one). On the addition however of free Pr_3P to the benzene solution of the cis-compound, isomerisation is very rapid.

(3) The addition of a bridged platinum compound capable of reacting with Pr_3Sb formed during the isomerisation of the stibine complex should on the basis of this mechanism strongly inhibit the isomerisation of the cis-Sb compound and this was found to be the case experimentally.

It is hoped to study further equilibria; the results obtained should throw light on the nature of the bond between the metal and the ligand.

DISCUSSION

In opening the discussion, Dr. Mann drew attention to the difficulties of this type of experimental work, and to the existence of $(PCl_3PtCl_2)_2$ which has been known for a very long time. In this compound the chlorine also would be expected to inactivate the donor properties of the phosphorus.

Dr. Anderson mentioned his own experience of this type of experimental work and that the idea of using d electrons from the metal had been foreshadowed by a number of workers including Hieber in its application to CO compounds. He was interested that these considerations led Dr. Chatt to prefer the ethylidene structure for olefine compounds. He raised a number of points:

(1) If the displacement of one olefin by another involved the switch of a hydrogen atom from one carbon atom to another then ought not such a mechanism to initiate polymerisation of the olefin, particularly of an olefin such as styrene.

(2) The relative stabilities of olefin compounds were determined by replacement reactions in which volatility of the olefin would

play an important part. It is not known whether styrene complexes are more stable than the ethylene complexes and he asked whether Dr. Chatt had any thermochemical data.

(3) He considered the relationship to the carbonyls well worth developing. The palladous carbonyls are very unstable and appear to decompose by two mechanisms depending on the particular ion involved:

(a) $[CO\,Pd\,Cl_3]^- + X^- = CO + [PdXCl_3]^-$

(b) $[CO\,Pd\,Cl_3]^- + 2X^- = X_2CO + Pd + 3Cl^-$

(a) occurs particularly with cyanide and nitrite (b) with the hydroxyl ion. Dr. Chatt may be able to use this as evidence for his structure.

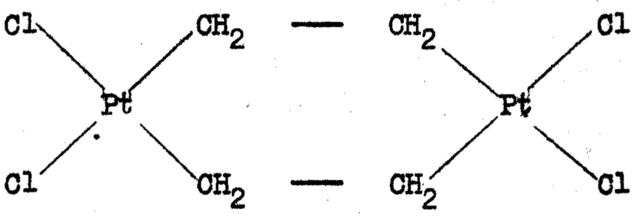
(4) In choosing nickel carbonyl for replacement of CO by PF_3, Dr. Chatt was unfortunate in his choice of carbonyl.

Replacements take place more readily in the polynuclear carbonyls and he suggested that iron tetracarbonyl be tried.

Dr. Palmer drew attention to the probable prevalence of double bonds in co-ordination and pointed out that the name dative double bond is rather formal, as once the bond is formed it is similar to any other double bond and no separation of charge is involved. He did not like the idea that one d-orbital on the platinum atom might contribute to the binding of two groups in the trans position. This was answered by L.E. Orgel, who showed that a weak binding to both groups was possible, as he would explain in his paper. Dr. Palmer also asked whether chlorination of olefin compounds had been attempted and what products were obtained. Dr. Chatt replied that the platinum atom was first chlorinated, then chlorine was taken up only very slowly and at elevated temperature when complete decomposition took place. Only ethylene dichloride was found, no ethylidene dichloride.

Prof. Sidgwick said that the co-ordination of carbon was one of the least understood problems of co-ordination, only recently had it been realised that carbon is a donor and not an acceptor. He mentioned the co-ordination of aromatic hydrocarbons and possibility that some of these might be clathrate compounds like $NH_3C_6H_6Ni(CN)_2$ investigated by Powell. A discussion followed in which it was shown that this structure for the carbonyls obeyed the inert gas rule exactly as the old structure.

Dr. Eley wondered whether there was evidence for or against structures of the type:



Dr. Chatt said he had considered this possibility (see Karasch and Ashford, J.A.C.S., 1936, 58, 1735) and shown that $CH_3C_6H_4NH_2$, C_2H_4, $PtCl_2$ was monomeric; therefore, the ethylene was attached to one platinum atom only. Dr. Anderson in discussing carbonyl compounds said any proposed structure had to explain:

(1) That the C — O distance is very different from that observed in ketones but similar to that in CO.

(2) The most stable carbonyls were those of group VI elements $M(CO)_6$. The double bond requires twelve links from the metal atom.

Prof. Wardlaw suggested that perhaps olefin compounds were clathrate compounds but this is shown to be incorrect by their stability in solution and the molecular weight determination mentioned earlier.

D.C. Bradley asked whether experiments with deuterium substituted ethylene CHD = CHD were contemplated. Dr. Chatt replied that the deuteration of ethylene platinous chloride was contemplated to see whether $CH_2D.CH_2D$ or CH_3CHD_2 was produced.

G.E. Coates asked whether the preparation of $Ni(PF_3)_4$ had been attempted by direct reaction of PF_3 with metallic nickel. Dr. Chatt replied that a negative result was obtained both in experiment at atmospheric pressure and in sealed tubes.

[Dr. Anderson's first questions were still unanswered; Dr. Chatt would like to record the following observations:

(1) Polymerisation of olefins is initiated by addition of a proton and even strong acceptor molecules, e.g. BF_3, does not

initiate the polymerisation of isobutene in absence of water or some similar substance (see A.G. Evans and G.W. Meadows, Trans. Far. Soc., 1950, 46, 327). Further evidence that movement of hydrogen atoms does not necessarily initiate polymerisation is provided by experiments of Fosches and Rideal who showed that the deuteration of ethylene on metallic nickel at >60°C. was a slower reaction than deuterium exchange with the hydrogen of the ethylene. This demonstrates extreme mobility of hydrogen atoms but they reported no polymerisation.

(2) We have no further data on stability but the argument developed in the paper requires only that the styrene, ethylene and butadiene complexes should have comparable stabilities and all the others should be less stable. The displacement experiment leaves no doubt about this.

(3) As to whether reaction (a) or (b) takes place depends upon the tendency of X^- which is known to enter the trans position, to form a dative double bond; if this is high, as with $-CN$ or $-NO_2$, the π bond to the CO is weakened and the carbon monoxide is liberated as such. If X^- does not affect the π bond then decomposition may occur, but the first stage need not be elimination of carbon monoxide but some addition compound of carbon monoxide may be found.

(4) Nickel carbonyl was chosen for these experiments because it is known that it is very difficult to replace all the carbon monoxide by any other ligand, and if we succeed in replacing it all by PF_3, we would have positive evidence that PF_3 and CO are very similar in their co-ordination. The only other substances to replace all the CO in nickel are the closely similar isonitriles (Hieber, Z., Naturforschungen, Vb, 129. (1950))].

SOME ASPECTS OF THE STEREOCHEMISTRY OF THE CO-ORDINATION NUMBER FIVE

By Prof. K.A. Jensen

(Copenhagen University)

Only very few compounds of elements exhibiting a co-ordination number of five have hitherto been prepared. The halides of the elements of group five, and iron pentacarbonyl, however, definitely prove the existence of pentacovalent elements. Although Langmuir discussed the formula $[PCl_4]$ Cl for PCl_5, the physical properties of phosphorous pentachloride and similar compounds (low melting point, solubility in non-polar solvents, low dipole moment and conductivity) are not in accordance with such a structure. For the spatial configuration of a compound of the structure YX_5 there are obviously three possibilities:

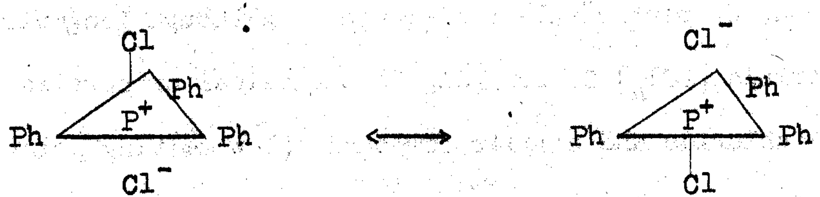
(a) The five bonds may be identical. This is only possible with a planar configuration.

(b) One of the bonds may be different from the four others.

(c) Two of the bonds may be different from the three others.

At one time Bergmann and others thought that the second possibility was realized in the halides PCl_5 and $SbCl_5$, both on chemical grounds and because they found finite dipole moments for these compounds. However, Simons and Jessup showed that if the atomic polarization is properly allowed for, the dipole moments of these compounds will be zero, and Linke and Rohrmann found the dipole moment of PF_5 to be zero by measurements on the gas over a wide temperature range. Accordingly the second possibility is ruled out, and these compounds must be either plane or have the configuration of a trigonal bipyramid. Electron diffraction measurements on a great number of pentahalides of phosphorous, niobium, tantalum and other elements are in accordance with the latter structure. It may also be mentioned, that some years ago I investigated the Raman-spectrum of antimony pentachloride and found 6 Raman lines, which is in accordance with the symmetry D_{3h}, the trigonal bipyramid, and definitely rules out the planar configuration, which should only have three active Raman-frequencies.

I further investigated compounds of phosphorus, arsenic, antimony and bismuth of the type $(C_6H_5)_3YCl_2$, where Y = P,As,Sb,Bi and found their dipole moments to be zero, if the atom polarization is properly allowed for. It should perhaps be mentioned, that I explained some of the properties of these compounds by assuming that polar resonance structures of the type:



have some importance. These structures become less important the higher the atomic weight of the element Y. These polar structures are in agreement with the octet theory. The octet principle, which is strictly obeyed for nitrogen, seems still to have some importance for the higher elements in group V especially for phosphorus and arsenic but less for antimony and bismuth. For example, it was found that the compound $Ph_3Sb(OH)_2$ is actually a dihydroxide, whereas the phosphorus and arsenic compounds with the corresponding empirical composition are hydrates of phosphine and arsine oxides, Ph_3PO,H_2O and Ph_3AsO,H_2O, i.e. their structure is in accordance with the octet rule.

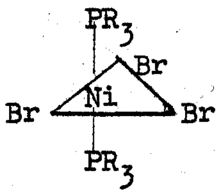
For the compound $(CH_3)_3SbCl_2$ Wells has shown the trigonal bipyramid configuration by X-ray measurements.

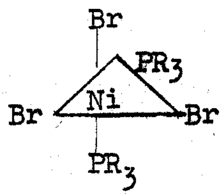
Accordingly this configuration seems to be fairly well established for several compounds of some pentacovalent elements, and it has been supposed that this configuration should be the normal one for all such elements.

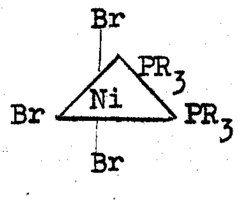
In the course of my investigations of nickel complexes of the type $[NiX_2(PR_3)_2]$ I observed that these red compounds easily add halogens or nitrogen dioxide to form dark blue (or green) complexes containing tervalent nickel. The compounds are rather unstable, but the bromide

[$NiBr_3(PEt_3)_2$] was isolated in a pure form and shown to be monomolecular in benzene solution. Recently Nygaard and I have submitted this compound to a closer examination and shown that its magnetic moment was 1.72 - 1.90 magnetons, in close agreement with the value computed for tervalent nickel, assuming that the magnetism is determined by spin alone.

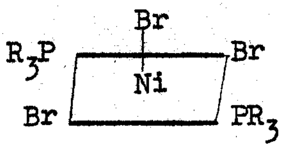
If this complex has the configuration of a trigonal bipyramid, there are three possibilities for the structure:



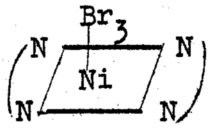




Of these the first should have a zero dipole moment and the two others should have very large dipole moments, because the phosphine molecules are in cis-position. Actually, the compound was found to have a dipole moment of 2.5 D. This seems to rule out the trigonal bipyramidal configuration, but is in accordance with a tetragonal pyramidal structure, derived from the original square trans-compound by addition of a halogen atom on one side of the square:



It would be very interesting to investigate this stereochemical question somewhat more closely, but the nickel compound mentioned represents a hitherto unique type of structure, so that the first problem was to investigate the possibility of preparing other compounds of that type. We have tried to add halogens, especially bromine, to a great variety of square nickel complexes, especially of the chelate type, but so far we have only in one case obtained a definite result: dimethylglyoxime nickel adds bromine, when it is suspended in non-polar solvents, e.g. CCl_4, to form a black compound, which we have shown to possess the formula $Ni(DH)_2Br_3$. With some of the other glyoxime nickel compounds similar complexes could be prepared. All these compounds are very unstable. With chlorine instead of bromine we also at first obtained a dark coloured precipitate, but the ligand was soon destroyed with the formation of diacetyl. The magnetism of the compound [$Ni(DH)_2Br_3$]was determined and found to be about 1.8 Bohr magnetons, which is in agreement with the supposition, that the compound contains tervalent nickel. We assume that the compound is formed by addition of a Br_3-group on one side of the square complex:



This black compound is easily soluble in sodium hydroxide and aqueous ammonia to form an intensely red solution. The formation of similar coloured solutions have previously been observed by precipitation of dimethylglyoxime nickel in the presence of oxidising agents, such as lead dioxide, hydrogen peroxide and others. Feigl has isolated a compound from these solutions, which was formulated as a compound with quadrivalent nickel: $Ni(DH)_2O$, but Okač and co-workers (Okač A., and Polster M., Coll. Czech. Chem. Comm. <u>13</u> (1948)561, 572) have shown that it is impossible to prepare a compound of this composition, the product isolated generally containing alkali, lead and other impurities. Okač thinks that it is the glyoxime moiety and not the nickel which is oxidised. Our experiments, however, may be interpreted simply in this way, that the tribromide is hydrolysed to give a compound of tervalent nickel with the formula $Ni(DH)_2OH$, which is soluble in alkali, e.g. by forming the complex $Ni(DH)_2(OH)_2^-$. As mentioned it has been impossible to isolate a compound of well-defined composition from these solutions, but we have found that the spectrum of the red solution formed from the bromide, measured in a Beckman spectrophotometer, is practically identical with the absorption spectrum of a solution formed by oxidation of nickel dimethylglyoxime with lead dioxide in alkaline solution.

So far we have not found other well defined compounds containing tervalent nickel. It should perhaps be emphasized that the phosphine bromide complex is the first well defined compound of tervalent nickel to be described. Some others had previously been reported, but a critical examination has shown that they do not in fact contain tervalent nickel. Thus it was shown by Malatesta (Malatesta L., Gazz. chim. ital., <u>70</u>, 842) that the nickel benzamideoxime compound of Dubsky and Kuraš (Dubsky J.V. and Kuraš M., Publ. Fac. Sci. Masaryk 1929, no.114) contained divalent nickel, whereas part of amideoxime moiety had been oxidised, and we have shown that the seemingly well-defined formoxime nickel complex of K.A. Hoffmann, (Hoffman, K.A., and Eberhard, U., Ber. <u>46</u>, (1913) 1457) $Na_3(Ni(CH_2NO)_6)$ is not a real tervalent nickel compound. To our great surprise we found this complex to be diamagnetic although according to its stoichiometry it should contain tervalent nickel. I shall not go further into our rather extensive researches on this and similar compounds, but mention that we here have a case similar to the compounds of quadrivalent antimony of the type $Rb_2[SbBr_6]$ which also are diamagnetic, although the complexes contain an odd number of electrons.

We have also tried to prepare cobalt compounds in which the central atom exerts a co-ordination number five. Cobalt forms phosphine complexes of the same type as the nickel complexes, e.g. $[CoCl_2(PEt_3)_2]$. These are blue and soluble in benzene. Their dipole moments are large and accordingly they cannot, as the corresponding nickel complexes have a trans-planar configuration. Magnetic measurements show them to contain three unpaired electrons. Hence, it is most plausible that the complexes have a tetrahedral configuration.

Whereas the corresponding nickel complexes easily add halogens the cobalt complexes were destroyed in this way. It was, however, found that nitrosyl chloride transformed them into complexes of tervalent cobalt:

$$[CoCl_2(PEt_3)_2] + NOCl \longrightarrow [CoCl_3(PR_3)_2] + NO$$

This compound is permanganate coloured and soluble in non-polar solvents, even in petroleum ether. Its magnetic moment shows it to contain two unpaired electrons, in accordance with the assumption that it contains tervalent cobalt with five covalent bonds. Its dipole moment was found to be about 2 D, a similar value as that found for the nickel complex. Thus we conclude that also this cobalt complex has a tetragonal pyramidal configuration.

The nickel compound $[NiCl_3(PR_3)_2]$ could be prepared as well by the action of nitrosyl chloride as by the action of chlorine on

$[NiCl_2(PR_3)_2]$.

Finally we have investigated the action of NO_2, which acts as $NONO_2$, on the nickel and cobalt phosphine complexes. From the red nickel chloride a dark blue nitrate is formed:

$$[NiCl_2(PEt_3)_2] + N_2O_4 \longrightarrow [NiCl_2(NO_3)(PE_3)_2] + NO$$

Its magnetic moment was found to be 1.7 Bohr magnetons, accordingly it contains tervalent nickel.

A corresponding cobalt compound could be prepared by the reaction of nitrogen dioxide with the complex $[CoBr_2(PEt_3)_2]$. Its colour was however, dark blue and not redviolet as in the case of the trichloride, and magnetic measurements showed it to contain four unpaired electrons, indicating the presence of cobaltic ions in the complex. Thus the bond type is not altered by forming the tervalent nitrate as it was when forming the chloride.

We are continuing our efforts to prepare more compounds in which the central atom exhibits the co-ordination number five, and intend to submit the stereochemical question to a closer examination when we have found some compounds more stable than those hitherto prepared.

The problem of the bond arrangement for the co-ordination number five has been treated by some authors from a quantum mechanical point of view. It is of interest that Daudel and Bucher conclude from their calculations that compounds of the type XY_5 should have the trigonal bipyramidal structure if the bonds involved are formed by s-, p- and d-electrons having the same principal quantum number, but the tetragonal pyramidal structure if the dsp-bonds are formed by means of d-electrons having a lower and s- and p-electrons having a higher principal quantum number. This is exactly the case with the nickel- and cobalt compounds described. Among previously described compounds only iron pentacarbonyl could have this structure.

Electron diffraction and infra-red spectroscopic measurements suggest that iron pentacarbonyl has the trigonal bipyramidal structure. I am not quite convinced by the experimental evidence, but it may be that this more symmetric structure is realised when all 5 ligands are identical.

GENERAL DISCUSSION

Professor Sidgwick remarked that all previously known 5-covalent compounds have a trigonal bipyramidal structure except iodine pentafluoride which is square pyramidal with the iodine not in the plane of the four fluorine atoms, but slightly above it and could the observed dipole moment of Jensen's complexes be due to the nickel atom being out of the plane of the phosphorus and two bromine atoms? Jensen replied that the nickel atom is at the most 0.1-0.2 A° above the plane of the four groups; any greater distance would produce a large change in the observed dipole moment because of the large moment of the Ni-P link.

Dr. Nyholm said that with Co(III) and ionic bonds there should be four unpaired electrons. However, even $Co_2(SO_4)_3$ and cobaltic alum are diamagnetic (paramagnetism sometimes reported probably due to cobaltous salt). Jensen's tervalent compound $CoCl_3.2Et_3P$ has four unpaired electrons and is apparently the first cobaltic compound which has been shown to have four unpaired electrons. It would be interesting to know whether measurements have been carried out on cobaltic fluoride. (No one appeared to know).

Irving remarked that although Daudel and Bucher had predicted the square pyramidal structure for dsp^3 hybridisation, it was probable that in fact **the ratios** of the various orbitals in the hybrid were fractional (see Duffey $d_{\frac{4}{9}}\ s\ p_{\frac{14}{9}}$ for strong square co-ordination).

THE SIGNIFICANCE OF d-ORBITAL HYBRIDISATION IN CO-ORDINATION COMPOUNDS

By Mr. L.E. Orgel

(Oxford University)

In this talk I want to describe certain applications of wave-mechanics to problems of d-orbital hybridisation. This work has been carried out by Dr. Craig, Dr. Maccoll, Dr. Sutton and myself. Since it is not possible, in a short talk, to deal both with the mathematical theory and with the results, I shall give only a brief qualitative account of the theory.

Atomic orbitals are classified as s, p, d, etc., according to the value of their second quantum number one. In the first short period of elements one s-orbital and three p-orbitals, corresponding to the principal quantum number two, are progressively filled up. In the next quantum shell there are an additional five d-orbitals available. Subsequent quantum shells include further numbers of f-orbitals etc. The order in which these orbitals are filled is well known to you if not to me. One point which should be remembered in connection with such atomic orbitals, is that in each quantum shell the occupied p-orbitals project more than the s-orbitals and the d-orbitals more than the p-orbitals. In treating theoretically the combination of atoms to form molecules two methods are much used. In the first, the Valence Bond method, unpaired electrons on two different atoms are paired together and are shown to lead to chemical bonding between the atoms. In the second method, that of Molecular orbitals, electrons are assigned to orbitals covering the whole molecule. In nearly all such treatments these molecular orbitals are obtained by adding together atomic orbitals on the different atoms to form suitable linear combinations. The point which I want to emphasise is that in both treatments the atomic orbitals appropriate to the bonded atoms are of fundamental importance.

Pauling suggested that the strength of a chemical bond depended on the orbitals on the bonded atoms being directed towards each other. He further showed that by combining the s, p, and d orbitals in various ways one could obtain sets of equivalent orbitals with very strong directional properties. These are the familiar sp_3 tetrahedral, dsp_2 square, d_2sp_3 octahedral arrangements. It can easily be shown that sets of orbitals directed to the corners of a square or the apices of an octahedral cannot be formed by using s and p orbitals alone, thus providing confirmation of the suggestion that d-orbitals are involved.

Pauling considered only the directional character of the atomic orbitals in his theory of bond strength. However, it now seems almost certain that their radial distribution is also very important in this connection. It will be remembered that atomic orbitals are usually treated as being the product of an angular and a radial function. The latter function determines how diffuse the orbital is, and is governed in part by the electronegativity of the atom.

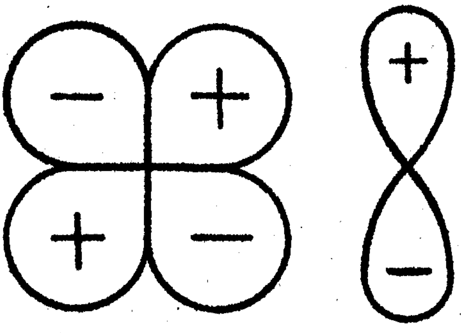
It is in general impossible to evaluate the integrals necessary to obtain the strengths of real bonds; so one is driven to seek for useful approximations.

A measure of the overlap of atomic orbitals which takes both factors into account is provided by $s = \int \phi_A \phi_B d\tau$ where ϕ_A and ϕ_B are natural orbitals on the two bonded atoms. This integral is called the overlap integral and measures the extent to which the two orbitals tend to occupy the same region in space. The overlap integral is in fact a quantity important both in the molecular orbital theory and the valence-bond theory. Mulliken has recently shown that for the not too ionic compounds of the two short periods, strong bonds are always associated with large overlap integrals. Maccoll has applied the same method to the different hybridised states of carbon with satisfactory results, which incidentally do not always agree with Pauling's theory.

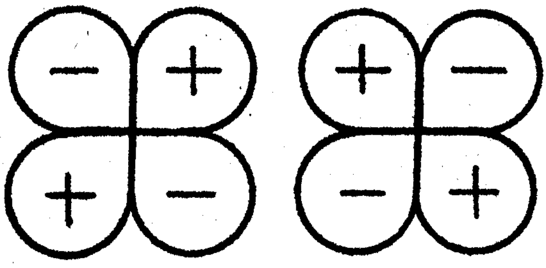
The overlap integral is in fact a measure of the build up of charge in the region between the nuclei and hence, provided it is true that the atomic orbitals for free atoms are suitable for building up the orbitals in molecules, it is easy to see why this integral is so closely connected with bond strength. We must note, however, that in bonds between atoms of very different electronegativity other sources of stabilisation than those provided by the overlap of natural atomic orbitals must be important. This is, of course, true to a lesser extent in all cases and is one of the reasons why overlap is only a qualitative measure of bond strength. There are also other theoretical reasons which show that overlap cannot be taken as a quantitative measure of the bond strength. Furthermore since the overlap integral contains no direct reference to the internuclear repulsion it cannot be expected to give quantitative information about bond length. Despite these drawbacks the values of the overlap integral should be useful as a source of qualitative information, that is information about the plausibility of certain kinds of bonding, or perhaps the range of electronegativity ratios for which strong, essentially covalent, bonds can be expected.

In the course of the work I am describing overlap integrals between 3s, 3p and 3d orbitals, corresponding to various types of bond, have been evaluated. As atomic orbitals we have used simple Slater functions, which consist of an angular factor multiplied by a radial function of the form $r^n e^{-\alpha r}$. They differ from the true atomic orbital functions in the absence of certain nodal surfaces; however, in the important outer region they are a good approximation to the correct function. The exponent α determines the "size" that is the diffuseness, of the orbital. Fairly accurate estimates of α for most of the lighter atoms can be made, either from theoretical calculation, or from spectroscopic data. In general the smaller the value of α, the larger is the orbital and the less the electronegativity of the atom.

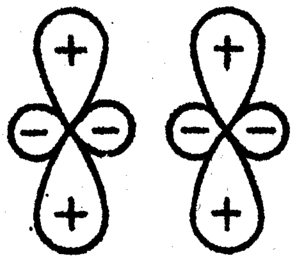
The kinds of bonding considered may be classified as single, double and delta- bonding. Single bonds between 3s-3p, 3p-3p and 3d-3p pairs of orbitals may be illustrated as follows:- Double bonding between $d_\pi - p_\pi$ and $d_\pi - d_\pi$. δ-bonding of two types as follows:



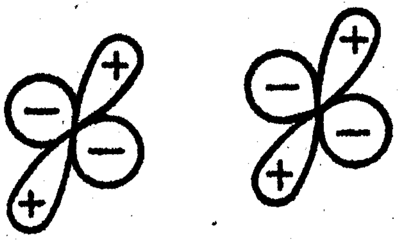
$\pi(d_\pi - p_\pi)$



$\pi(d_\pi - d_\pi)$



$\delta(d_{z^2} - d_{z^2})$



$\delta(d_{xy} - d_{xy})$

for each of these bond types we have evaluated the overlap integrals corresponding to all important ratios of the α' values for the two different atomic orbitals. In cases where hybridisation is of interest we have also found overlap integrals for the more important hybrid orbitals.

It will be convenient to distinguish between two rather different cases of d-orbital hybridisation. In the first the available d-orbitals belong to the same quantum shell as the s and p orbitals. This case includes molecules such as phosphorus pentachloride and sulphur hexafluoride. In the second case the available d-orbitals are in the shell below that of the other bonding electrons. The complexes of the transition metals often fall into this class of compounds, although $[CoF_6]^{4-}$ and similar compounds probably belong to the first case.

In the case of single bonds we find, if we compare the magnitude of s-p, p-p and d-p overlap integrals, that at small internuclear separations the d-orbital overlap is rather smaller than the corresponding overlap for s and p orbitals. However, at rather larger distances this difference becomes insignificant. Hence there is no reason to believe d-orbitals less capable of bonding than s and p orbitals. Another point which is of some interest is that overlap is greatest for $d_{z^2} - p_\delta$ bonding when the d-orbital is rather less electronegative than the p-orbital. Differences of electronegativity in the opposite direction cause a rapid fall off in the overlap.

In a typical molecule, the formation of which requires the use of promoted d-orbitals, say PCl_5, we may find the α-value of Cl by means of some empirical rules first suggested by Slater. Similarly the s and p orbitals of phosphorus can be assigned α-values with some confidence. If we then try to find the range of α-values for the d-orbital which will allow strong overlap with the chlorine atom and at the same time will hybridise effectively with the s and p orbitals of phosphorus, we are led to a value much larger than that given either by spectroscopic studies or by a rather doubtful extension of Slater's rules. Whether this is to be explained by assuming that electronegative atoms alter the α-value of a central atom or whether it indicates an inadequacy of the overlap method in dealing with bonds involving promoted electrons is not certain. However, since this subject is not very closely connected with co-ordination chemistry we will not pursue it further here. It is perhaps worth mentioning that in these calculations on phosphorus pentachloride we do find that the overlap is a maximum at a rather larger internuclear distance in the axial bonds than in the radial bonds, although the actual magnitude of the overlap is little different.

The formation of hybridised d-bonds by the transition metals presents no new theoretical difficulties. Although Slater's rules would suggest that α for the central metal is larger for the d-orbitals than for the p-orbitals, this is not true in practice. It is quite clear from the spectroscopic properties of the free atoms that the d-orbitals bore almost the same energy as the s and p orbitals. This provides very good evidence to show that the α-values for the two types of orbital are quite similar. We will assume this to be true in our discussion of single bonds.

An adequate discussion of these transition metal bonds must involve a knowledge of 4s-4p and 4p-4p overlap integrals. Mulliken's table of s and p overlaps, formerly supposed to contain all useful s and p overlap integrals up to the fifth quantum shell, fails to include just these integrals. We have, therefore, calculated them for the equicentre case, and in so far as we need them in other cases we replace them by 3s-3p, 3p-3p overlaps. This alters the numerical values slightly but still shows the general trends of the overlap integral for hybridised orbitals.

The maximum value of the overlap integral for octahedral bonds is .54 and occurs at a bond length a little greater than that for the maximum overlap in tetrahedral bonds. The maximum value of the overlap for tetrahedral bonds is .51. Now this result is very different from that predicted by Pauling's bond strength criterion. It will be remembered that according to Pauling the bond strengths are in the ratio of 2.94 to 2.00.

This discrepancy between the two theories is quite general and perhaps of some importance. It will be remembered that on the Pauling theory the s orbital has a bonding strength of unity, the p orbital a strength of 1.72 and the last p orbital is sp_3 with a bond strength of 2.0. It has long been realised that this theory does not fit all the facts. Thus there is considerable evidence to show that in carbon the strongest bonds are formed, not by sp_3, but by sp orbitals. Maccoll calculated the overlaps of various s-p hybridised orbitals corresponding to the case of carbon and finds that the s-p bond gives the best overlap. Hence there is some reason for believing that the overlap picture is nearer the truth than Pauling's theory. In the chemistry of co-ordination compounds too I imagine that the ratio 2.92-2 exaggerates the difference in strength between tetrahedral and octahedral bonds, if there is any systematic difference.

The actual values of maximum overlaps for different bonds are probably not as significant as the values of the different overlaps at the same internuclear distance, since bond lengths do not in general correspond to the distance of maximum overlap. However, if we take overlap at a given bond length we reach substantially the same conclusion, namely that the change in strength on going from tetrahedral to octahedral co-ordination is not greater than five or ten per cent at any likely bond-length.

Considering next the π and δ bonds we can say immediately that our calculations suggest that δ bonding is most unlikely. For all electronegativity ratios the overlap is extremely small at bond lengths as large as those which occur in octahedral complexes.

Nyholm has suggested that d_π orbitals may be used by phosphorus and arsenic to form double bonds with a central metal. Such compounds would involve d_π-d_π overlap. In the normal way we would expect the exponent for the d_π orbital on the metal to be much greater than that on the phosphorus or arsenic atom. However, in these compounds we must remember that the phosphorus or arsenic atom has used its inert pair of electrons in forming a covalent bond and hence its effective electronegativity towards a d-electron will be much larger than it would be in the free atom.

The actual values of the d_π-d_π overlap are quite large, the maximum overlap being as high as .35. Furthermore, the fall off of the overlap as the electronegativity ratio increases is slow. In fact it remains quite large for all plausible values of this ratio.

Furthermore in this particular case overlap calculations almost certainly underestimate the importance of double bonding, since in the formation of double-bonds there is incidentally a charge transfer in the opposite direction to that accompanying the initial single-bond formation. Thus in a sense the occurrence of d_π-d_π double bonding increases the stability of the single bonds by providing a mechanism which removes excess of charge from the central atom.

Thus to summarise, if d_π-d_π binding occurs at all, Nyholm's complexes should be ideal cases. On overlap grounds such bonding seems probable.

The other interesting case of double bonding in transition metal complexes, is that between d_π orbitals of the central metal and p_π orbitals of attached atoms or radicals. Experimental results are available for a large number of cyanides, nitrosyls etc. The stability and properties of these compounds have, for a long time, been attributed to such double bonding. Nearly all the interesting cases involve the $2p_\pi$ orbitals of carbon and nitrogen. However, we may interpret their properties in terms of $3d_\pi$-$3p_\pi$ overlap without serious error.

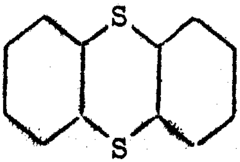
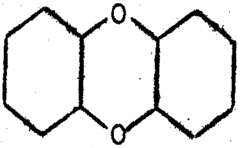
The $2p_\pi$ orbitals in carbon will correspond to an α-value not very different from that of the d-orbital of the central atom, so we will simplify our treatment by considering the equicentre case only. At bond lengths corresponding to those observed, the overlap integral has a value of about .15. It is interesting that this is rather larger than the overlap integral between two $3p_\pi$ orbitals at the same distance. From symmetry considerations we can show that if d_π orbitals are used in square complexes, then two strong π- bonds will be formed at right-angles to one another. Similarly in octahedral complexes three strong bonds should be formed perpendicular to each other. In fact the experimental evidence on this point is not conclusive.

Certainly as we have heard there are cases where the trans form seems the more stable. On the other hand Syrkin's work, which is admittedly a kinetic study, does seem to be in agreement with perpendicular double bonds. It must be remembered that our calculations refer only to the double-bond structure and take no account of σ-bond effects or of the possible effects of steric hindrances.

Finally, I should like to mention the possibility of d_π-p_π hybridisation. In just the same way as σ-orbitals may be combined to give directed bonds, we can hybridise d_π and p_π orbitals to give directed π-bonds. In this way we can increase the magnitude of the overlap to quite a considerable extent. Such hybridised bonds would be inclined to each other at an angle of between 90° - 120°. The greater the d_π contribution, the smaller would the inter-bond angle be.

This kind of hybridisation might occur in dsp_2 square complexes, where the $3d_\pi$ orbitals could combine with the $4p_\pi$ and so on.

In addition there is a considerable amount of evidence to show that such $d_\pi p_\pi$ hybridisation does in fact take place in many aromatic sulphur compounds

In this way the non-planarity of  in contrast to the planar structure of  and the similarity of thiophene to benzene may be explained. Dr. Craig has pointed out that the ultra-violet spectrum of diphenyl sulphide can most easily be explained in terms of π bonds inclined at a small angle to each other.

Finally I would like to say again that these calculations are at the best qualitative. They cannot give bond energies or bond lengths.

DISCUSSION

Dr. Palmer said that L.E. Orgel talked a great deal of "hybridisation" but he thought there was a lot of misunderstanding of the word. If you take a carbon atom with unhybridised orbitals and put an electron into each, the electronic distribution is spherically symmetrical. The same applies to the octahedral distribution, it makes no difference whatever to the carbon and is the same whether the orbitals are hybridised or not. Hybridisation is purely formal and only exists in ones mind, it has no physical counterpart at all. L.E. Orgel agreed that charge distribution was spherical and quoted Leonard Jones as having said that apart from the total distribution of charge, one is interested in the electrons separately. Bonds are formed which kept electrons in one bond away from those in another. Although the total charge is symmetrical it is not exactly the same whether hybridised or not.

Dr. Chatt asked if the calculations give any reason why nitrogen which cannot form a double bond with platinum is also subject to labilisation by groups of marked trans influence. L.E. Orgel replied that if the Pt-N bond is a plain σ-bond he could not explain this behaviour.

CO-ORDINATION GROUPS OF ATOMS IN CRYSTALS

By Dr. A.F. Wells

(I.C.I. Dyestuffs Division)

The general arrangement of the bonds formed by an atom in a particular state of valency is now known in many cases, though it is to be expected that the interbond angles will vary somewhat according to the nature of the attached atoms. For symmetrical bond arrangements (e.g. 4 coplanar bonds) one would expect to find the "ideal" bond angles in a molecule or complex ion of the type AX_n in which n similar atoms or groups are attached to the central atom A. In chelate compounds, in which a complex group of atoms is attached at two or more points to the central atom, the situation may be complicated by the geometry of the chelate group, and similarly in a polynuclear complex $A_mY_nX_p$ the bond angles of A may be affected by the requirements of the bridging atoms Y. This last complication is likely to occur in many crystals, for the crystal structure of a compound represents a compromise between the requirements (as regards interbond angles and size factors) of two or more kinds of atom. A further complication is that in an extended 3-dimensional structure there must also be relations between the numbers of bonds formed by an atom of a given sort and the proportion of that type of atom in the structure. These points will be illustrated by reference to the crystal structures of compounds of Pd, Pt and Cu.

The deviations from what we may describe as the "ideal" bond angles for a given valency state vary from small distortions, as in a series of crystals such as PtS, PdS and CuO, to a completely different bond arrangement as in Be and Co phthalocyanines. In the former case the structures are all of the same general type but of progressively lower symmetry; in the latter, metals which normally form four tetrahedral bonds are obliged to form four coplanar bonds because of the geometry of the rigid organic molecule.

The stereochemistry of divalent copper in crystals is of particular interest because, except in the case of compounds such as hydrated oxy-salts, and also some co-ordination compounds with organic molecules which are isomorphous with argentic compounds, the structures of its compounds are unique and not isomorphous with the corresponding compounds of any other metal. Cupric oxide has been mentioned above. The sulphide has a rather extraordinary structure which might well be re-investigated. The structure of CuF_2 is not known, but it is known that it is not the fluorite or rutile structure. The chloride and bromide are isomorphous and closely related to $PdCl_2$, though differing in the way in which the infinite chains are packed. This difference is such as to give Cu two more distant Cl neighbours in addition to the four nearest coplanar neighbours, these completing a distorted octahedral co-ordination group. The next nearest neighbours of Pd in $PdCl_2$, on the other hand, are a set of four at the corners of a rectangle the plane of which is perpendicular to that of the four nearest neighbours. This group of (4 + 2) neighbours appears in all the halogen compounds of divalent copper and has been discussed elsewhere (A.F. Wells, J.C.S., 1947, 1662, 1670). In the "basic" cupric salts in which there are generally two sets of crystallographically non-equivalent Cu atoms, other environments occur, according to the published structures. This was the case in, for example, atacamite, $Cu_2(OH)_3Cl$, but a redetermination of the structure (A.F. Wells, Acta Cryst., 1949, 2, 175) shows that in this crystal also all the Cu atoms have the characteristic set of (4 + 2) neighbours. Similarly, a redetermination of the structure of malachite (A.F. Wells, Acta Cryst., in the press) confirms that Cu^{II} has this type of environment in this hydroxy-carbonate. In CuO the Cu atoms have only four oxygen neighbours, the next nearest neighbours being a set of four copper atoms. However, in a crystal AX, the number of bonds formed by A must necessarily be the same as that formed by X (assuming all A atoms to have the same environment and similarly for all X atoms) so that in this case the failure of Cu^{II} to form (4 + 2) bonds is presumable due to the fact that O cannot form (4 + 2) bonds. Compounds containing 6-co-ordinated Cu^{II} such as $[Cu\ en_3]X_2$, which are described in the literature, would appear to be exceptions to the (4 + 2) co-ordination, but no detailed information about their structures is available, and the resolution of the tartrate of $[Cu(H_2O)_2en_2]^{2+}$ has not been confirmed by later work.

DISCUSSION

Dr. Mann said that the six-covalent ammonia and ethylenediamine copper complexes were relatively unstable and although triaminopropane would with, for example, zinc, combine to form a six-covalent complex, copper formed a compound with triaminopropane which still contained four-covalent copper.

Dr. Wells stated that Prof. Sidwick (in "Chemical Elements and their Compounds") described a six-covalent complex of copper with ethylene diamine, with formula $(Cu(en)_3)Br_2$ but Dr. Wells did not know whether the compound was particularly stable.

Prof. Jensen described some recent work by Bjerrum and Nielsen who determined the consecutive formation constants of the diethylenediamine cupric ion and the third consecutive complexity constant. The results indicated that the triethylenediamine complex is a pentammine complex with the ethylenediamine molecule last taken up bound by only one of its amino groups.

Prof. Schwarzenbach amplified Prof. Jensen's statement by giving the values for the consecutive formation constants $k_1 = 10^{10}$; $k_2 = 10^{19}$ and $k_3 = 10^{-1}$. It was extremely difficult to get any attachment of the third molecule. The values for the addition of ammonia showed a similar gradation.

Prof. Albert mentioned some of his own work on copper complexes. He said that if glycine is added to copper sulphate in solution then the soluble blue copper diglycine complex is obtained. If then phenol is added to this solution, large violet crystals separate and these contain two molecules of glycine and two molecules of phenol per atom of copper. Is this not a hexa-covalent copper complex? Admittedly, hexacovalent copper has never been encountered <u>in solution</u>.

Dr. Mann said that this complex would have to be investigated further before this question could be answered.

Dr. Wells further stressed the peculiarities of the crystal chemistry of copper. He said that all simple copper (II) compounds have a different structure from that of the other metal compounds, e.g. copper sulphide was [illegible] any other simple sulphide.

Dr. Chatt said that following up Prof. Albert's statement, Malcolm Crawford has recently described a number of cupric salts of organic acids which did not dissolve in alcohol or in benzene unless a little alcohol was added. The crystals obtained in some cases retained the alcohol and in some cases did not.

Dr. Wilkins mentioned cupric bromide wihch had been studied recently by Helmholtz. Four bromine atoms were arranged planar around the copper and a further two were at a slightly greater distance. This was another compound which fitted in with Dr. Well's ideas on the stereochemistry of copper. He also drew attention to some work by Peyronel who prepared the solid compounds $Cu(NH_3)_6Cl_2$, $Cu(NH_3)_6Br_2$ and $Cu(NH_3)_6I_2$ and showed an octahedral co-ordination of the complex cations.

SUMMARY

by Dr. L.E. Sutton

(Oxford University)

In summing up, Dr. Sutton called attention to three groups of contributions: the preparative and experimental developments, the equilibrium and rate studies, and the theoretical investigations.

One of the most striking general features of the first group was the difference in the standard of discussion resulting from the clearer appreciation in the past ten or twenty years of the usefulness of physical methods, and especially of the need for prefacing speculation about the structure of solid compounds by an X-ray crystallographic examination. Measurements of electric dipole moment are useful for structural determinations in the gas-phase or in non-polar solutes: but there is a marked lack of a satisfactory method applicable to aqueous solutions. Electron diffraction is also a powerful tool for examining free molecules.

Of the topics being actively investigated, he was struck by the importance of finding out more about the formation and stability of bridged groupings such as occurred in the complexes or crystals described by Dr. Mann and Dr. Wells, which are fundamental building units in many instances.

Dr. Chatt's speculations about the ethylene complexes were very interesting; and he hoped that more conclusive evidence bearing on them would be obtainable. The new relations between stereochemistry, valency states, and bond types developed by Prof. Jensen and by Dr. Nyholm were striking and important.

The contributions on equilibrium measurements showed that a pleasing degree of accord exists between workers who have attacked the problem with rather different aims in mind. Prof. Schwarzenbach dwelt on the simple, fundamental features of equilibria common to all complexes and concerned particularly with the stereochemical nature of the ligands; Dr. Irving emphasised the specificity of central atoms. But there was no serious disagreement in their conclusions. The desirability of obtaining internal energies of formation of complexes was immediately obvious; the difficulties of doing so were, however, considerable. Little had been said about rates of formation and decomposition save by Dr. Wilkins, by Prof. Schwarzenbach and by Dr. George: but this was the next major field of investigation and the results seemed likely to require considerable changes in our present ideas.

Dr. Well's discussion of problems of solid structure was a timely one. We had a great deal of information about such structures: we needed clearer and more complete statements of the reasons why they happen.

The theoretical contributions by L.E. Orgel, in association with Dr. Craig and Dr. Maccoll, illustrated the difficulties which characterise such work at present. The broad simple generalisations were made about twenty years ago by Pauling. We knew that in many respects they were too simple; but it proved difficult to make useful improvements. Although this means that progress was gradual, it was steady; and in a while we should probably find that our general understanding of valency had improved very considerably.

To make the discussion definite, its scope had been limited to co-ordination in the older sense of definite and stoechiometric reaction between supposedly "saturated" molecules or ions. As techniques of investigation have improved more kinds and degrees of interaction have been observed: so the limits of what may be called co-ordination chemistry - if we allowed the term to cover all kinds of molecular interaction - were continually becoming wider and more nebulous. This circumstance made it necessary to watch theoretical developments carefully. The interrelations of the various phenomena are such that an attempt to answer one problem might well throw light upon what seems at first a quite different one. We could not be sure that we had all the main principles established, and although we hoped that we had we might still see fresh forms of valency discovered and fresh kinds of interaction revealed.

In conclusion Dr. Sutton conveyed the very warm congratulations of all present to Professor Sidgwick on the publication of his monumental work, which they would for long regard as the chemist's Bible.

LIST OF GUESTS ATTENDING THE SYMPOSIUM

Prof. A. Albert	National Univ. of Australia, ~~[illegible]~~.
Dr. J.S. Anderson	Harwell.
Mr. D.C. Bradley	Birkbeck College, E.C.4.
Dr. F.H. Brain	Guy's Hospital Medical School.
Dr. A.R. Burkin	Southampton.
Mr. F.H. Burstall	C.R.L. Teddington.
Miss I.G.M. Campbell	Southampton.
Mr. G.E. Coates	Bristol.
Dr. W.A. Cowdrey	I.C.I. Dyestuffs.
Dr. D.P. Craig	University College, W.C.1.
Dr. P.J. Durrant	Cambridge.
Dr. D.D. Eley	Bristol.
Dr. R.C. Evans	Cambridge.
Dr. M.E. Foss	Guy's Hospital Medical School.
Dr. P. George	Cambridge.
Dr. N.W. Hansen	I.C.I. Paints.
Dr. H. Irving	Oxford.
Prof. K.A. Jensen	Copenhagen.
Mr. H.R. Leech	I.C.I. General Chemicals.
Dr. W.J. Lile	Mid Essex Technical College.
Dr. A. Maccoll	University College, W.C.1.
Dr. F.G. Mann, F.R.S.	Cambridge.
Dr. R.B. Mooney	I.C.I. General Chemicals.
Dr. R.S. Nyholm	University College, W.C.1.
Mr. L.E. Orgel	Oxford.
Dr. W. Palmer	Cambridge.
Dr. G.A. Rowe	I.C.I. Dyestuffs Division.
Prof. G. Schwarzenbach	Zürich.
Prof. N.V. Sidgwick, F.R.S.	Oxford.
Dr. L.E. Sutton, F.R.S.	Oxford.
Prof. W. Wardlaw, C.B.E.	Birkbeck College, E.C.4.
Dr. A.F. Wells	I.C.I. Dyestuffs.