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THE PRESENT STATE AND FUTURE DEVELOPMENT OF CO-ORDINATION CHEMISTRY

A.A.Grinberg

CONTENTS

I. Importance of applications of co-ordination chemistry 334
II. Importance of quantitative parameters in co-ordination chemistry 335
III. Mutual influence of co-ordinated groups 336
IV. Directions of development of classical co-ordination theory which are still important 337

I. IMPORTANCE OF APPLICATIONS OF CO-ORDINATION CHEMISTRY

The name "co-ordination chemistry" shows that this branch of chemistry was based on Werner's co-ordination theory, but considerable development has taken place from the theory put forward in 1893 to co-ordination chemistry as it stands today. About forty years ago, at the time of Werner's death, co-ordination theory dealt with material which was regarded as part of inorganic chemistry and included a group of compounds whose compositions could not be explained satisfactorily by classical valency theory.

The chemistry of complex compounds was regarded as an extremely specialised branch of chemistry and many organic and physical chemists considered it unnecessary to become familiar with it. Gradually, however, it became apparent that co-ordination theory was of great importance for the development of adjacent fields of science, and as a result, co-ordination chemistry ceased to be merely a branch of inorganic chemistry and became a field of interest to inorganic, organic, analytical, and physical chemists, biochemists, chemical crystallographers, and technologists in different fields. It first became clear that complex compounds were extremely important for developing analytical chemistry, and an important part was played by Chugaev, whose work on dioximes[1] laid the foundation for the systematic application of co-ordination complexes in qualitative and quantitative analysis. Dimethylglyoxime, dicyandiamidine[2], cupferron[3], and α-nitroso-β-naphthol, proposed for the determination of cobalt[4] as early as 1885, were the first successful examples of the use of organic reagents in chemical analysis.

It would be difficult now to list briefly the reagents proposed for qualitative detection or quantitative determination of individual elements. The methods of applying the reagents have also become extremely varied, and extend beyond their use for precipitation and colour reactions. Of particular importance is the use of complex-forming ligands in combination with extraction and ion-exchange methods. These processes are finding ever-increasing application for the separation and purification of lanthanides and actinides. Also we have the sequestering agents, which make it possible to bind complex-forming metals as very stable soluble complexes and so eliminate the catalytic influence of their ions on processes of technological or biochemical interest[5]. It is well known that the technology of the platinum group metals is entirely based on the use of complex compounds, and that the principal process for extracting gold from its ores (cyanide process) is also based on complex formation.

It has recently become clear that complex compounds are of considerable importance as catalysts or intermediate products in a variety of organic syntheses[6]. The change in the reactivity of organic ligands accompanying complex formation with a metal is particularly important. It is also important that the product formed by the organic molecules or ions with the complex-forming metal should be sufficiently labile to allow the process to occur again. Some examples of processes of practical importance where complexes act as catalysts are: (a) catalytic oxidation of

hydrocarbons under the influence of cobalt(II) salts, involving the intermediate formation of peroxides and free radicals; (b) the so-called "oxo-reaction", that is the reaction of olefines with carbon monoxide and hydrogen to form aldehydes [this takes place under the influence of cobalt and involves the intermediate formation of complexes such as $Co_2(CO)_8$ and $HCo(CO)_4$ – in the analogous Fischer–Tropsch synthesis iron carbonyls formed as intermediate compounds act as catalyst]; (c) hydration of unsaturated compounds, as in the Kucherov reaction, by which acetylene is converted to acetaldehyde in the presence of mercury salts; (d) condensation of olefines and acetylene derivatives under the influence of nickel carbonyl or nickel cyanide (Reppe); (e) preparation of vinylacetylene by dimerisation of acetylene in solutions containing copper chloride (Berk and Klebanskii); and (f) polymerisation of ethylene and its analogues by Ziegler's method using catalysts formed by the reaction between titanium tetrachloride and aluminium trialkyls.

These examples show the importance of complexes in organic synthesis. They must also be exceptionally important in processes taking place in animal and vegetable tissues. The part played in biology by such typical complex compounds as haemoglobin and chlorophyll is well known. When we consider that insulin is a zinc complex, vitamin B_{12} one of cobalt, the phenoloxidase enzymes complexes of copper, and the catalases and peroxidases complexes of iron, it becomes clear that complex formation is closely related to important vital processes. We could also quote illustrations of the importance of co-ordination chemistry in the development of crystal chemistry and radiochemistry, but the above examples suffice to emphasise that the *applications* of modern co-ordination chemistry are increasing rapidly and continuously. The combined theoretical and practical importance of co-ordination chemistry apparently explains the great interest shown in this branch of chemistry by young students.

II. IMPORTANCE OF QUANTITATIVE PARAMETERS IN CO-ORDINATION CHEMISTRY

A second characteristic of modern co-ordination chemistry is its gradual transformation to a strictly quantitative science. Hein has stated[7] that Werner's theory was the last great purely-chemical theory. The theory itself contains no calculation, apart from the enumeration of the isomers to be expected from octahedral or planar models of complex ions. For the solid state, X-ray structure analysis has not only confirmed the correctness of Werner's models but has also made them more definite by giving the values of the interatomic distances and bond angles. In the case of solutions, it is interesting that even as early as the end of the nineteenth century Abegg and Bodländer had introduced the concept of instability constants and pointed out several approaches to a quantitative estimation of the stability of various complexes. This pioneer work, however, remained obscure for a long time.

In the first decade of the present century, the concept of instability (or stability) constants was used systematically by a few workers, including Niels Bjerrum. The energy effects accompanying the manifestation of secondary valency were at first characterised quantitatively by thermochemical and tensimetric measurements; the vapour pressures of ammines of various metals were measured at different temperatures by Isambert, Ephraim, and more particularly, W.Biltz.

A quantitative theory of stepwise complex formation in solutions was given by J. Bjerrum in his classic paper of 1941.[8] He developed this theory and also an experimental procedure applied to the formation of ammines and amine complexes in aqueous solution. Systematic studies on the determination of stepwise constants in solutions of acido-complexes were carried out at about the same time by Babko[9]. The work of Bjerrum and Babko was the starting point for a vast number of determinations and methods of calculation of instability constants in aqueous solutions of complexes of a number of metals. They marked a new stage in the development of co-ordination chemistry. In addition to Bjerrum's method for finding stepwise constants of complex formation in solution, methods were put forward by Leden[10] and Fronaeus[11]. All these methods are applicable to stepwise complex formation provided that only mononuclear complexes are present in the solution. Sullivan and Hindman[12] have made a comparison and critical analysis of Bjerrum, Leden, and Fronaeus' methods for finding stepwise constants.

The experimental data necessary for calculating the constants can be obtained by potentiometric, conductometric, spectrophotometric, distribution, or ion exchange methods. Certain other methods can also be used, including polarography, developed in Czechoslovakia. Each method has special features which must be taken into account and the reliability of the results is naturally higher if they are confirmed by independent methods. A fairly large amount of data on stepwise formation constants for complexes of many metals with various ligands has now been accumulated.

In a few cases measurements have been made at different temperatures, making it possible to characterise the separate stages of complex formation by the thermodynamic quantities ΔG, ΔH, and ΔS. The accumulation of these data is exceptionally important, since it makes possible a complete thermodynamic characterisation of the tendency for a central ion to form complexes with ligands of very different chemical character. This should lead to a detailed analysis of the relation between the position of an element in the Periodic Table and its tendency to form complexes. As a first approximation, this relation has been established using a statistical approach[13]. On the other hand, these quantitative data on the stability of complexes raise new and extremely interesting problems concerning, for example, the factors determining the relative magnitudes of the stepwise constants of complex formation and the relation of these factors to the electronic structures of the complex-forming metal and ligand and hence to the nature of the bond in the complex.

In dealing with polybasic acids, each subsequent proton is, as a rule, more difficult to remove than the preceding one. However, within the limits of this effect, understandable in terms of electrostatics, individual acids show very large differences in the values of the successive constants. In the case of complexes consisting of a charged central ion and neutral ligands, the stepwise dissociation of the ligands is not accompanied by a change in the charge on the complex ion, so that there is no apparent electrostatic factor which might hinder the removal of ligands after the first. Examination of the available data on the stepwise dissociation of complexes of this type shows that in many cases the ratio of the successive constants is fairly close to that required by the statistical effect. Sometimes, however (for example with mercury(II) ammines), there is a very marked difference in the values of K_4 and K_3 on the

one hand, and K_2 and K_1 on the other. In some cases (silver ammines), the first stability constant K_1 is found to be even smaller than K_2, thatis, the attachment of a second ammonia molecule to the $AgNH_3^+$ ion leads to a marked increase in the stability of the co-ordination compound[8].

The case of silver ammines is not unique, and it is clear that the ratios of the successive constants and the factors on which they depend require further study. These relations should reveal a functional dependence on the nature of the co-ordinate bond in the individual cases, and should probably be analysed using the molecular orbital and ligand field theories. In the author's opinion, the crystal field theory and even the simpler electrostatic and polarisation theories still have a part to play in the chemistry of complex compounds. It is of course true that the molecular orbital theory is more rigorous and probably closer to reality, but the difficulties associated with its application to actual systems will, for some time, make it necessary to resort to crystal field theory, particularly in its improved form (ligand field theory)[6,14,15] and even to the less refined polarisation theories. Any theories based on the unmodified picture of an isolated central atom and isolated ligands can of course only approximately reflect the actual relationships.

The theory of stepwise complex formation was developed for the analysis of systems containing mononuclear complexes. Much work on methods for their synthesis and determination of their structures was done by Werner himself[16]. In extending the ideas of Bjerrum, Leden, Fronaeus, and others, the Swedish chemist Sillen[17] evolved an experimental procedure for the study of hydrolytic and polymerisation equilibria in solution leading to the formation of polynuclear complexes. The procedure of Sillen and coworkers establishes unambiguously the existence of polymerisation equilibria and makes it possible, without isolating the products from solution, to determine their composition and the constants for the separate stages of the dissociation.

Sillen's procedure is essentially a form of physicochemical analysis and this work introduces substantial changes in current theories of the nature of the hydrolysis products of salts of a number of metals and is of great importance in examining the complex nature of equilibria in solutions of borates, vanadates, chromates, etc. The successive and overall instability constants in solutions of platinum complexes are being systematically studied in our laboratory[18-19].

All this shows that the thermodynamics of complex formation is being extensively developed and will continue to be for many years. In the USSR it is being systematically studied by Babko, Komar', Yatsimirskii, and others. For several years the author has held the view that our ideas on the chemical behaviour of complex compounds will be complete only when we have enough information on both the thermodynamics and kinetics of complex formation. This is particularly true of the most typical and characteristic complex-forming species, for which the reactions of substitution and exchange in the co-ordination sphere take place relatively slowly.

The kinetics and mechanism of complex formation are now being studied in a number of laboratories. In England, Ingold's school, which has done much work on the mechanism of organic reactions and introduced the concepts of the S_N1 and S_N2 reactions, has taken up the study of exchange and substitution in cobalt(III) derivatives. Systematic studies of the kinetics of substitution in cobalt(III) derivatives are being made in the USA by Basolo and Pearson, who have developed the theory of the so-called S_N1CB mechanism, and also by Adamson and his pupils. The conclusions reached by English and American workers regarding the mechanism of these reactions show some disagreement.

Important kinetic studies on the trans effect in Pt^{II}, Pt^{IV}, and Rh^{III} derivatives have been made by Gel'man[20] and Zvyagintsev and Karandasheva-Shubochkina[21], and the kinetics and mechanism of exchange and substitution reactions in platinum derivatives are being systematically studied in our laboratory[22]. Some work on this topic has been done in the USA by Banerjea, Basolo, and Pearson[23] and by Elleman and Martin[24,25]. Interesting work on the kinetics and mechanism of redox reactions involving complex ions has been done in the USA by Taube, who has also attempted to classify complex ions as "labile" and "inert". One of his most interesting results is the discovery of the intermediate formation of bridged complexes of the type $(NH_3)_5Co^{III}Cl...Cr^{II}(H_2O)_5$. In these reactions the oxidation is accompanied by migration of a co-ordinated anion from the oxidising agent to the reducing agent[26]. Interesting work by Jezowska-Trzebiatowska's school[27] in Wrocław (Breslau) has shown that an increase in the rate of reduction of permanganates and ferrates by hydroxyl ions takes place on the addition of alkali metal cations, which apparently act as bridges, facilitating the approach of ions with charges of the same sign.

Work by the present author, Gil'dengershel' and In'kova has shown that some substitution reaction in the co-ordination sphere of Pt^{IV} derivatives involves intermediate redox processes[28,29], and additional data confirming these results were obtained in work with Kukushkin[30]. A general conclusion from our studies of the kinetics of exchange and substitution in Pt^{II} derivatives is that the lability or inertness of complexes is determined not only by the nature of the central atom and the co-ordination type of the complex, but also by the nature of the ligand and the solvent in which the reaction takes place. Studies by Taube[31] and Dreyer[32] indicate that another factor is the presence of catalysts, which can accelerate or retard isotopic exchange.

A second general conclusion is that the kinetics of isotopic exchange and substitution in Pt^{II} derivatives are not always determined by their thermodynamic characteristics. On the contrary, more stable complexes often undergo exchange and substitution reactions much more rapidly than those less stable[33,34]. This applies not only to platinum derivatives. Brown, Fallab, and Erlenmeyer[35] found that when α,α'-bipyridyl reacts with iron(II) and copper(II) salts, the less stable iron(II) complex is formed first and is converted to the more stable copper complex only after several hours. In the case of platinum derivatives, these characteristic relationships can be explained by the mutual influence of the co-ordinated groups.

III. MUTUAL INFLUENCE OF CO-ORDINATED GROUPS

Chernyaev's discovery[36] in 1926 of the trans effect was an exceptionally important addition to co-ordination theory. As he himself said of the trans effect, "it introduces the elements of dynamics into the pure geometry of Werner's theory".[37] The co-ordination theory, which made it possible to predict the number of isomers for any complex ion composition, did not indicate methods for the synthesis of these theoretically-possible iosmers. Chernyaev's rule

gave chemists a means of predicting the direction of reactions in the co-ordination sphere and of synthesising compounds with a required structure. The theoretical essentials of the trans effect have not yet been revealed completely.

Recent experimental results have made it possible to characterise the trans effect quantitatively as a kinetic effect[21], but there are also data indicating that it has a thermodynamic aspect[38-45]. The recent attempts by Chatt[46], Cardwell[47], and Orgel[48] to explain the trans effect are essentially applicable only to the kinetic effect in Pt^{II} derivatives, but the trans effect is also shown in octahedral complexes of atoms other than Pt^{II}.

Of all the attempts which have been made to explain the trans effect, the most general is perhaps the suggestion that it is due to a redox interaction between the central ion and the ligand[49]. This interaction leads to an increase in the electron density between the central ion and the trans--active ligand. The interaction between the central ion and the group in the *trans*-position to the active ligand is changed and as a result the properties of this group approach those of a group in the unco-ordinated state. The old Nekrasov–Grinberg polarisation model is a particular case of this general theory.

It is possible that in Pt^{II} derivatives the presence of an electron pair capable of forming a dative bond is another factor intensifying the trans effect. In any case the study of the mutual influence of groups in the co-ordination sphere of various central ions is one of the most important problems in modern co-ordination chemistry. This importance is further emphasised by the fact that, as shown in our laboratory, co-ordinated groups may also influence kinetics and thermodynamic properties when present in the *cis*--position (the cis effect)[22]. Moreover, different workers hold different views on the relative magnitude of the trans effect shown by ligands attached to Co^{III}.[6,50-52]

IV. DIRECTIONS OF DEVELOPMENT OF CLASSICAL CO-ORDINATION THEORY WHICH ARE STILL IMPORTANT

For a long time after the co-ordination theory was put forward, attention was mainly directed to the stereochemistry of complexes with co-ordination numbers six and four. We have at present data on the stereochemistry of many elements in different oxidation states. The stereochemistry of Pt^{IV} was developed to an exceptional extent by Chernyaev's school[53-55]. Bailar's school made the first attempt to apply conformational analysis to the stereochemistry of complex compounds[56].

Of particular interest is the stereochemistry of those elements for which different degrees of oxidation correspond to different co-ordination numbers, and also of elements for which the spatial distribution of the co-ordinated groups depends on the chemical nature of the ligands. The stereochemistry of large ions, which can have a co-ordination number greater than six, is also interesting. In this connection attention should be directed to systematic studies of the stereochemistry of the lanthanides, actinides, and alkaline earth elements; such work has already begun in the Radium Institute and the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences. In its further development purely chemical studies will have to be combined with physical methods for determining structures. The work of Debye and Scherrer, Dickinson, Cox, Belov, Bokii, Porai-Koshits, Hanic, Rasmussen, Rundle, and others has already shown the important part played by direct X-ray diffraction methods in the determination of the structure of complexes.

If we do not restrict stereochemistry to stereostatics, the range of problems is extremely wide and should include all phenomena associated with the relation between chemical and physical properties of complex compounds and their spatial configuration.

In addition to stereochemistry, another very important problem of classical co-ordination chemistry is that of the acid–base and redox properties of complex compounds. Studies carried out over a number of years in our laboratory show that the features observed in the manifestation of acid–base properties by geometrical isomers may vary, depending on the mobility of the proton in the co-ordinated ligand and on the mutual influence of the co-ordinated groups. The fact that the acidity of U^{IV} derivatives is greater than that of Th^{IV} derivatives is of considerable interest. The importance of studies of the redox properties of complexes has already been mentioned: many years ago in our laboratory it was found that complexes of the platinum metals, in addition to stepwise secondary dissociation with the removal of co-ordinated ions or molecules, showed another characteristic property of complex ions, *viz.*, redox interaction between the central ion and the ligands leading to reduction of the central ion and removal of the oxidised form of the ligand[57,58]. Thus for the PtX_6^{2-} ion, for example, dissociation according to the scheme $Pt^{IV}X_6^{2-} \rightleftharpoons Pt^{IV}X_5^- + X^-$ is accompanied by dissociation according to the scheme $Pt^{IV}X_6^{2-} \rightleftharpoons Pt^{III}X_5^{2-} + X^0$. Measurement of the redox potentials of systems composed of PtX_6^{2-} and PtX_4^{2-} ions, together with a knowledge of the normal potentials of the $Pt^{4+} + 2e \rightleftharpoons Pt^{2+}$ and $X_2 + 2e \rightleftharpoons 2X^-$ systems, enables a quantitative relationship between these types of secondary dissociation of the complex to be established. Systematic studies on the influence of complex formation on the redox potentials of systems formed by a central ion and ligand are being made in the USSR by Fridman[59,60].

An extremely important direction of study in modern co--ordination chemistry is the synthesis and properties of such complex compounds as the carbonyls, the nitrosyls, compounds containing unsaturated olefinic or acetylenic ligands, the complexes, synthesised by Chatt and coworkers, containing co-ordinated hydrogen atoms[61], complex hydrides, and complex organometallic compounds of various types. Many of these types of compound are of considerable practical importance. We would merely refer to special new ligands like 1,8-bis(salicylideneamino)-3,6--dithiaoctane, first synthesised by Dwyer and Lions[62] (the co-ordination capacity of these ligands is six), and a number of new complexes prepared by Schwarzenbach's school and by Czechoslovak chemists. Particular mention may be made of the work of Majer, Dvořak, and Strugar[63], who prepared racemic and meso-forms corresponding to 2,3--diaminobutanetetra-acetic acid and stilbenediaminetetra--acetic acid.

The further study and application of these complexes, together with the use of optically-active ion exchangers, may be of wide theoretical and practical interest, and we may conclude, with Syrkin[64], that the synthesis of new types of complex may be extremely important in the further development of the theory of the chemical bond.

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Khlopin Radium Institute,
the USSR Academy of Sciences

SORPTION AND ION EXCHANGE ON AMPHOTERIC OXIDES AND HYDROXIDES

G. M. Zhabrova and E. V. Egorov

CONTENTS

1. Applications of amphoteric oxides and hydroxides as inorganic ion exchangers and sorbents. 339