

ALFRED WERNER

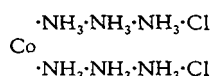
On the constitution and configuration of higher-order compounds

Nobel Lecture, December 11, 1913

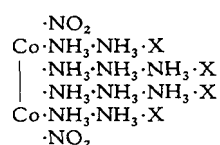
Allow me first of all to express my deeply felt gratitude to the Swedish Academy of Sciences for the distinction granted to me and for the honour of being invited to present to you an account of the progress of our knowledge concerning the structure of the molecules.

I started my scientific work by putting forward a hypothesis on the arrangement of atoms in nitrogen-containing molecules. In the years that followed, the hypothesis has borne much fruit; but I must refrain from discussing it in detail here, because the experimental confirmation of the conclusions to be drawn from it is the merit of my teacher, A. Hantzsch. In the same way I wish to make passing reference only to the ideas put forward in my treatise "Beiträge zur Theorie der Affinität und Valenz" (Contributions to the theory of affinity and valence) because the conclusions to be drawn from them are only now beginning to exert their expected influence. I shall limit myself to a discussion in detail of those of my researches which are concerned with the constitution and configuration of compounds to which little attention was given twenty years ago, by contrast with earlier times, i.e. the constitution and configuration of the so-called molecular compounds. During the great era of development of organic chemistry, during which the theory of structure was perfected, the molecular compounds had become stepchildren, and attention only continued to be given to a few of them because they were of practical interest. This neglect can be ascribed to the fact that it was impossible to develop the constitution of these compounds on the same valence principle as the constitution of organic compounds. It must therefore be stressed all the more that one of the most important groups of molecular compounds, i.e. metal ammonias, were carefully tended at that time in Sweden, by C. W. Blomstrand and P. T. Cleve. These two scientists had recognized the theoretical importance of these compounds whose characteristics had prompted Berzelius to number them with the "paired compounds". The former contributed to the knowledge of these compounds in the theoretical, the latter in the experimental respect.

Blomstrand directly followed Berzelius by putting forward certain concepts about the manner in which the components of the paired compounds are linked with one another in the molecules of these compounds. He followed the model provided by the constitution formulae of paired organic compounds, i.e. he arranged the components in the form of chains. To the compound $\text{CoCl}_2 \cdot 6\text{NH}_3$ for example he gave the following constitutional formula:



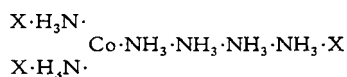
It was however known even in Blomstrand's day that in certain of these addition compounds of ammonia and metal salts, the individual acid residues can possess different functions, in that some have a firmer, others a looser bond. Blomstrand adapted his formulae to this fact by postulating that the firmer were linked with the metal atom, whereas the looser were the terminal members of the ammonia chains. For the xantho salts, for example, he derived the following formula:



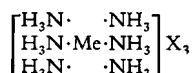
in which a double cobalt atom was assumed to be present in accordance with the view then prevailing.

For further progress in the knowledge of the constitution of metal ammonias we are again indebted to a Nordic scientist, i.e. the Danish chemist S. M. Jorgensen, who extended and deepened the field of metal ammonias by researches which have become classic. Jorgensen showed that the formulae containing double metal atoms are untenable, and that not only one, but two acid residues can be directly linked with the metal atom. He was further able to show that on the departure of one molecule ammonia from the compounds richest in ammonia - which always contain six ammonia molecules for one metal atom, and in which all the acid residues are in loose linkage - one acid residue, and, on departure of two ammonia molecules, two acid residues enter into direct bond with the metal atom. From this he concluded that these two acid residues in the hexammine salts of the tri-

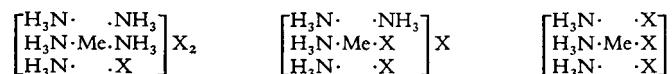
valent metals are only separated from the metal atom by interposition of one ammonia molecule each, from which he derived the following formula for the hexammine salts:



This was the stage of development of the theory of the constitution of metal ammonias when I began to deal with these compounds. From an examination of the behaviour of the compounds I recognized that in the event of the departure of a further ammonia molecule, the third acid residue also enters into direct bond with the metal atom. This, however, is only possible if in the hexammine salts this acid residue, too, is only separated from the metal atom by an ammonia molecule. Further I discovered that the other ammonia molecules also can be replaced by acid radicals which enter into direct bond with the metal atom. From this I concluded that the ammonia molecules cannot be connected chainwise at all, but must all be directly linked with the metal atom. The following formula therefore had to be derived for the hexammine metal salts:



and the following formulae were derived for the compounds formed from the above by ammonia loss:



That other metal ammonias, e.g. the platinum ammonias, chromic ammonias, etc. must have analogous formulae, was shown by their chemical behaviour.

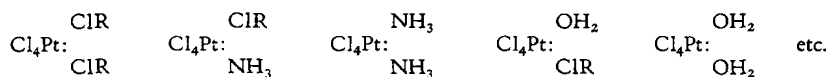
The diverse function of the acid residues in the compounds under discussion could, in accordance with the electrolytic theory of dissociation put forward by your famous member, Professor Arrhenius, also be interpreted by postulating that the acid residues in direct bond with the metal atom do not dissociate in solution, whereas those not directly linked with the metal atom occur as independent ions. It should be possible, therefore, to provide experimental physico-chemical evidence for the conclusions drawn, by de-

termining the electrolytic conductivity. The result of the investigation I carried out jointly with my friend A. Miolati, fully confirmed our conclusions, since we discovered that the compounds of which it was assumed that they contained all acid residues in direct bond with the metal atom, are so little dissociated electrolytically, that they behave practically as non-conductors. This important result was later confirmed again by an investigation carried out jointly with Ch. Herty. In this way we had secured an experimental foundation on which the new theory of the constitution of inorganic compounds could be based. The new theoretical principle which formed the guiding theme in the evaluation of constitution, can be summarized as follows:

Even when they are saturated in the sense of the older theory of valence, the elementary atoms still possess sufficient chemical affinity to bind other seemingly also saturated atoms and groups of atoms, under generation of clearly defined atomic bonds. This doctrine has now been so amply confirmed experimentally by investigations of a very large number of molecular compounds which are now called complex compounds, that we can make it the starting-point of further developments.

The first question to which we have to find an answer is that as to the number of atoms which can be directly linked with an atom forming the centre of a complex molecule. It has been found that this number which has been called the maximum coordination number is dictated by the nature of the mutually interconnected elementary atoms. Hitherto, the maximum coordination numbers, four, six, and eight have been observed, which corresponds to the theoretically possible symmetrical groupings of a corresponding number of points about a centre, if the neighbouring points are equidistant. It must however be noted that the composition of the complex chemical compounds must not invariably correspond to the maximum coordination number of the centre atom, because there are coordinatively unsaturated atoms, just as there are valence-chemically unsaturated atoms.

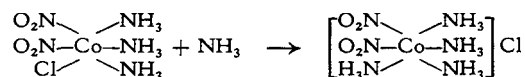
In inorganic chemistry, the coordination number six plays a predominant part, which finds expression in the predominance of complex compounds with complex radicals (MeA_6). On examining any binary compound whose centre atom has the coordination number six, we would therefore expect that it is capable of adding new components, until the coordination number, six, of the centre atom is satisfied. This conclusion has been confirmed experimentally. Let us select platinum tetrachloride as a simple example. It forms e.g. the following addition compounds:



whose constitutional formulae were established by detailed investigations. The formulae show that the compounds previously classified as double salts, and also the metal ammonias and the hydrates are wholly in agreement constitutionally, and that there are intermediate types which belong both to the one and to the other group. I have been able to confirm these constitutional relationships by demonstrating mutual transformation of the compounds in many cases.

All compounds which, like the derivatives of platinum chloride mentioned above, are formed by simple addition, are now classified as addition compounds. They represent one of the principal groups of higher-order compounds. Within the scope of this lecture it would be impossible even to attempt to show to you how extensive are the experimental facts which it has been possible to classify consistently theoretically on the basis of the views put forward. For the sake of general orientation, I only wish to add that the behaviour of platinum chloride recurs in an identical manner in a wide range of first-order compounds.

The addition compounds are joined by a second group of higher-order compounds, i.e. the intercalation compounds. These form when, as a result of the incorporation of a new component, the acid residues of a compound are displaced from the direct bond with the metal atom. The following is an example:

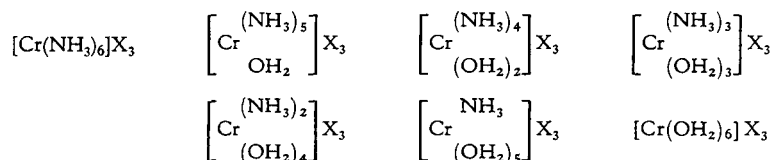


This completely changes the function of the acid residue, because after addition of ammonia it functions as an ionogenic group, whereas previously its bond was non-ionogenic. This prompts the assumption that after the addition process the acid residue is situated in a second linkage sphere in which it is enabled to form ions. With the assistance of electrical conductivity we were able to trace by measurements the process of intercalation in a large number of cases and, consequently, to establish experimental foundations for the evaluation of the formation of such intercalation compounds. The addition process with change of function of acid residues can be repeated until all acid residues are in ionogenic bond. We thus come to the end types

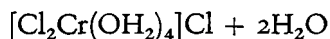
of intercalation compounds, which, with the metal ammonias, include the hexammine salts, with the examination of which we started. We must therefore visualize such a hexammine salt as a metal atom in the first sphere of which six ammonia molecules or amine molecules are linked by means of nitrogen, whereas the acid groups are situated in a second sphere. In the formula, we express this as follows:



In the metal ammonias, the ammonia molecules may in part be substituted by water molecules, and the water plays the same part in these compounds as ammonia. This doctrine is of fundamental importance, and I have therefore devoted a large number of papers to proving it. We may now consider it as proved, because we now know almost unbroken transition series from the metal ammonias to the compounds of metal salts with water, which latter are merely the hydrates of the metal salts. One of these transition series, in which only one link is missing, is known e.g. for the salts of tri-valent chromium:

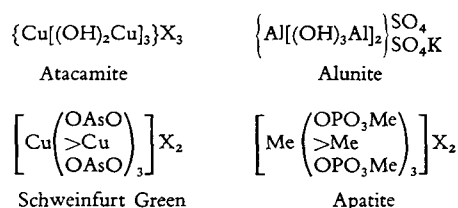


Since the water in the hydrates therefore plays the same part as the ammonia in the metal ammonias, it would be expected that on the withdrawal of water from the hydrates, individual acid residues belonging to the compound will also suffer a change in function. This conclusion, too, was experimentally confirmed, and, on that occasion, we discovered the cause of the difference between blue and green chromic chloride hexahydrate. We were able to show that blue chromic chloride is normal hexaquo chromic chloride, whereas the green chromic chloride corresponds to the following constitutional formula:

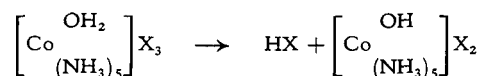


The isomerism is therefore based on a different mode of linkage of the water of hydration, and this kind of isomerism has therefore been called "hydrate isomerism".

Knowledge of the nature of the hydrates of metal salts has acquired great importance. The demonstration that the water molecules in the hydrates can be replaced by substituted water molecules, belonging to which metal hydroxides $\text{Me}(\cdot\text{OH})_2$ and metal oxygen salts can also be interpreted, rendered possible the opening up of the field of so-called multi-nuclear compounds. A large group of these compounds, in which metal atoms are mutually linked in a non-ionogenic manner by the oxygen of radicals such as OH, OAc, etc. has considerable importance in inorganic chemistry and in the chemistry of minerals. The constitution of basic salts such as atacamite, langite, alunite, etc. and that of the group including Schweinfurt Green, the apatites, etc. was clarified; they are in excellent concord with the constitutional formulae of the simpler compounds, as the formulae below show:



The study of the aquo-ammonia metal salts has also led to important results. The property of these compounds to have an acid reaction, and their ability to be converted into so-called hydroxo compounds, such as



has thrown new light on the process of hydrolysis, also on the nature of bases, and the process of salt formation. For it was found that, depending on the nature of the centre atoms and of the groups linked with them, these hydroxo compounds may exhibit very diverse characteristics. They may go through the whole scale from wholly neutral to strongly basic character, and this is due to the fact that the hydroxyl groups linked with the metal atom have a smaller or greater tendency to bind the hydrogen ions present in the water in small amounts. The greater this tendency, the more strongly basic are the hydroxo compounds. We thus obtain a new definition of bases, i.e. that the bases are compounds which have the ability to bind the hydrogen ions of the water, and in this way to disturb the equilibrium between the water and its ions by absorbing hydrogen ions, which results in an increase

of hydroxyl-ion concentration. Hydrolysis is based on partial cleavage of the aquo-salts into hydroxo compounds and acids, and salt formation on the formation of aquo-salts by addition of acids to hydroxo compounds. The knowledge of the behaviour of aquo-salts also provides the theoretical foundation for the evaluation of the constitution of oxonium salts.

Having sketched some of the principal areas in which the coordination theory has yielded a civilizing hand and has imposed order on the almost unconceivable multiplicity of the higher-order compounds that have accumulated in the course of time, I wish to discuss briefly the nature of the affinity forces bringing about the formation of these compounds. I have called these affinity forces secondary valences, to distinguish them from those called primary valences which bring about the formation of first-order compounds. In spite of the vast amount of experimental data we are not yet able to characterize precisely the difference that exists between the two types of valence. Most recent investigations have however shown that there is no fundamental difference between primary and secondary valences and that both types of valence have entirely the same significance for the cohesion of the atoms in the molecule. This leaves only the possibility of a gradual difference. I consider this gradual difference to be that the changing quantity of affinity which corresponds to a primary valence is sufficiently great to link an electron, whereas the affinity amount of a secondary valence is too small for this. As a consequence of this, the processes brought about by primary valences between atoms may be accompanied by electrical phenomena, whereas this is not the case with those caused by secondary valences.

In examining the coordination compounds we have so far taken account only of the affinity relationships between the atoms belonging to the atomic cluster, but have neglected the mutual positions of these atoms in the molecules. We are now concerned with the question as to the manner in which the six groups which in the complex radicals MeA_6 are linked with the centre atom, are arranged about this atom in space. This question can be answered by experimental examination of the consequences arising from the various possibilities of arrangement with regard to the occurrence of isomerism phenomena. That the arrangement of the six groups about the centre atom must be symmetrical, is rendered experimentally probable by the fact that in spite of many experiments we have never been able to observe isomerism phenomena in compounds with complex radicals : $[\text{Me}_6\text{A}]$. Of symmetrical arrangements, the following may be involved : (1) plane, (2) prismatic, (3) octahedron (Fig.I).

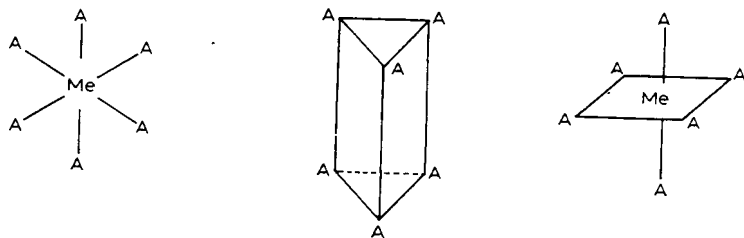


Fig. 1.

Plane and prismatic arrangements require, for compounds with complex radicals $[\text{Me}_{\text{A}_4}^{\text{B}_2}]$, the occurrence of three isomeric forms, whereas the octahedron arrangement only envisages the existence of two isomeric compounds of this nature (Fig. 2). The latter isomers are characterized in that one form contains the two B groups in two adjacent positions of the octahedron arrangement, whereas the other form contains it in more remote (diagonal) positions.

The experimental investigations have shown that compounds with complex radicals $[\text{Me}_{\text{A}_4}^{\text{B}_2}]$ do in fact occur in two isomeric forms; in no case were

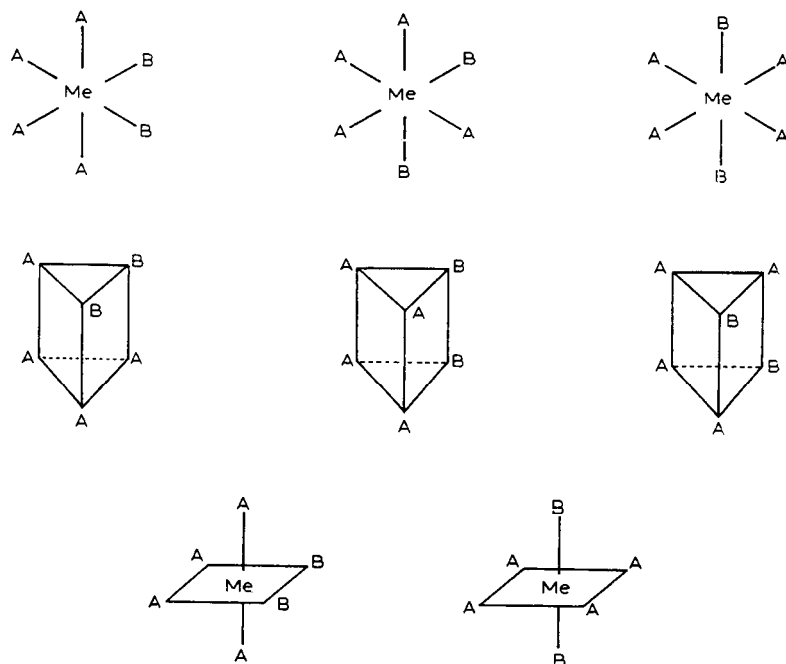
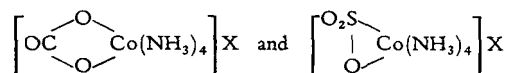


Fig. 2.

three isomeric forms found to exist (see Fig. 2). The elucidation of these isomerism phenomena which were discovered first in the platinum series and then in the cobalt series, occupied my mind for many years, and a large number of compounds had to be prepared to provide the material by means of which we were able to test the theoretical conclusions. Without this extensive material of compounds it would have been quite impossible to obtain information about the arrangement of the atoms in these molecules. We now know, in the case of cobalt, more than 20 different series of compounds which show this isomerism, and P. Pfeiffer has shown that identical isomerism phenomena occur in chromium. The differences in the properties of the isomers are so great that it is frequently possible to distinguish between them by external appearance. The difference e.g. between dichloro compounds: $[\text{Cl}_2\text{MeA}_4]\text{X}$ is particularly characteristic, both in the cobalt series and in the chromium series; they differ in that some isomers are green, and the others are violet. For some considerable time however such isomers were as a rule demonstrated only in compounds which contain amines, e.g. ethylene diamine, and it was therefore claimed with some semblance of justification that carbon was important for the occurrence of the isomerism phenomenon. I was however able to show that even the simplest compounds, the dichloro-tetrammine cobalt salts $[\text{Cl}_2\text{Co}(\text{NH}_3)_4]\text{X}$ exhibit this isomerism, which precluded any possible explanation other than that provided by the spatially different arrangement of the groups.

Configuration allocation, i.e. the determination in which isomers the two B groups are in the *cis*-position and in which isomers they are in the *trans*-position, was also carried out. We started with the consideration which also serves for the configuration determination of *cis*- and *trans*-isomers in organic chemistry, that groups in the *cis*-position are suitable for ring closure, whereas this is not the case with *trans*-groups. It was found that from compounds which, in the place of the two B groups, contain one group occupying two coordination points, e.g. the carbonate-sulphite group, etc.:



there were always obtained, on replacement of these groups by chlorine, bromine, etc., compounds of the violet series, although as a rule these are relatively unstable under the reaction conditions and will therefore be converted into the more stable, green *trans*-compounds on being subjected to these reaction conditions for some time.

During the preparation of metal ammonias which occur in *cis*- and *trans*-forms, from other stereo-isomeric metal ammonias by substitution reactions, i.e. by reactions in which certain groups are replaced by others, we found that rearrangements frequently occurred, in that *trans*-forms are formed from *cis*-compounds, and *cis*-compounds from *trans*-isomers. We can summarize this by saying that a change in position frequently occurs in substitution processes, so that the substituent group does not come to occupy that position in the molecule previously occupied by that displaced by substitution. These observations resulted in a new view of the progress of substitution processes. The entry of a substituent occurs as a result of the attractive affinity effect of the centre atoms, and the position the entering substituent seeks to occupy in the new atomic constellation is entirely independent of the bond position of the atomic group displaced by the substitution process. This concept which is indispensable for the explanation of the change of position during the conversion of stereo-isomeric inorganic compounds, has led to an explanation of the strange processes which occur in so-called Walden inversions, i.e. in the mutual inversion of mirror-image isomeric carbon compounds. In applying the concepts obtained for substitution processes in inorganic compounds to the conditions obtaining in carbon compounds, it is possible, without any secondary hypothesis and in a simple manner, to explain why, in substitution processes, either the spatially identically constructed molecules, or their mirror-image forms can occur.

The octahedral distribution of the six groups about the centre atom means that compounds with complex radicals



also must occur in two stereo-isomeric forms, according to the arrangement of the three B groups in a plane or in a sectional plane of the octahedron (Fig. 3).

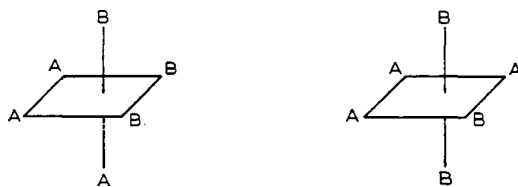
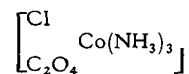


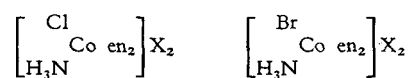
Fig. 3.

This conclusion also has recently been confirmed. The compound:



for example, exists in two isomeric forms, of which one is indigo blue and the other violet. With respect to the phenomena of the so-called geometrical stereo-isomerism, all the conclusions drawn from theory have been confirmed in such a perfect manner that there can be no further doubt as to the correctness of the theory.

The octahedral system permits other isomerism phenomena to be predicted apart from those we have discussed. Where the six groups linked with the centre atom are not all identical, molecular configurations can be derived which cannot be superimposed on their mirror images. It was therefore to be expected that the compounds corresponding to these molecular configurations would occur in optically active mirror-image isomers. In this lecture I shall merely discuss briefly a few cases which have been confirmed by experimental investigation. If we imagine four of the positions in the octahedral arrangement to be occupied by two coordinatively bivalent groups in a manner such that the two unoccupied positions are adjacent, and if we place two groups A and B in these positions, two spatial constructions become possible whose relationship to one another is that of two mirror-image forms which cannot be superimposed on each other (Fig. 4). Compounds which satisfy these conditions include the following:



We therefore attempted to resolve such compounds into optically-active mirror-image isomers. In many cases, this proved to be possible. The stability of the active forms is not, as I had at first feared, small, but the active

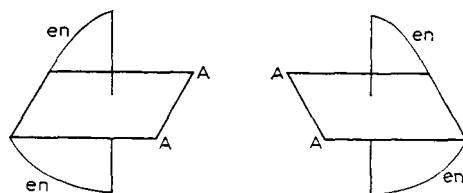


Fig. 4.

compounds are in part infinitely durable, and many are highly stable even in aqueous solution. In the case of the compounds under discussion, we can discover, in their molecular structure, an asymmetric cobalt atom of similar structure to the asymmetric carbon atom. This is however not the case in compounds with complex radicals: $[\text{en}_2\text{CoA}_2]$, with two A groups in adjacent positions. Even in this case, image and mirror image cannot be superimposed (Fig. 5). It was therefore of great interest to examine whether op-

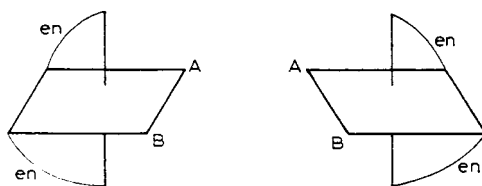
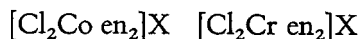


Fig. 5.

tical isomerism can also occur in compounds of this kind. Experiment confirmed it. Both in the case of cobalt and of chromium we were able to resolve into the mirror-image isomers the *cis*-dichloro-diethylenediamine compounds having the following constitutional formulae:



Further, we were able to resolve the *cis*-dinitrodiethylenediamine cobalt salts and the *cis*-diamine-diethylenediamine cobalt salts into the active forms, and the active carbonate- and oxalo-diethylenediamine cobalt salts were also obtained. In agreement with theory, it has however up to now proved impossible to resolve the corresponding *trans*-forms into active components in a single case, despite all our efforts to do so. In these compounds, we thus discovered conditions in molecular structure such as Pasteur in his day considered himself justified in assuming for the structure of all molecules, i.e. that the molecules consist in one symmetrically constructed and in two asymmetrically constructed forms, the latter of which behave like image and mirror image, and cannot be superimposed.

If we imagine the six positions in the octahedral system to be occupied by three coordinatively bivalent groups, e.g. ethylenediamine, we obtain a construction which cannot be superimposed on its mirror image either, although all six positions are occupied by chemically corresponding groups (Fig. 6).

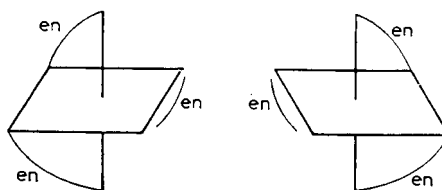
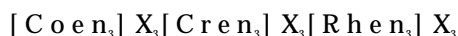


Fig.6.

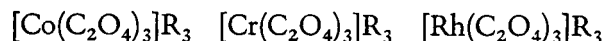
In this case, the asymmetrical structure of the molecules is thus wholly dictated by the spatial arrangement of the groups, and is entirely independent of the nature of the groups linked together. It therefore appeared to be particularly important for our conceptions of the origin of the optical activity of chemical molecules to establish whether such asymmetrical molecular structure also results in optical activity. This is in fact the case. In four different metals we succeeded in resolving compounds of this kind into optical isomers, i.e. in the case of cobalt, chromium, rhodium, and iron. For the first three metals we obtained in optically active form the triethylene-diamine compounds:



for iron, the tri- α -dipyridyl compounds:



Recently, we have begun a search for other similarly constructed compounds. We have been able to resolve into active forms, and in this way to establish beyond doubt the constitution of the metal trioxalic acids, compounds which correspond to the general formula:



This opens up much-promising prospects for the treatment of new fields of inorganic chemistry. May it be granted to me to justify the confidence which the Swedish Academy of Sciences has placed in me by the award of the Nobel Prize, by making further advances in the field of inorganic constitution research. In concluding allow me to express to you my gratitude for the kind attention you have given to my lecture.