

Alfred Werner

On the Constitution and Configuration of Higher-order Compounds ¹

Nobel Lecture, December 11, 1913

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.

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

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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 coordinated 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.

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 the gradual difference. I consider the 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 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. The question can be answered by experimental examination of the consequence 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

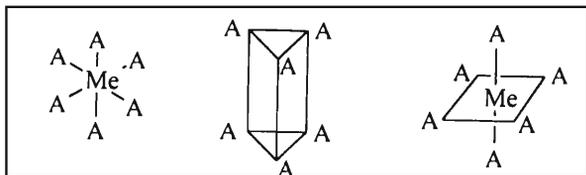


Figure 1.

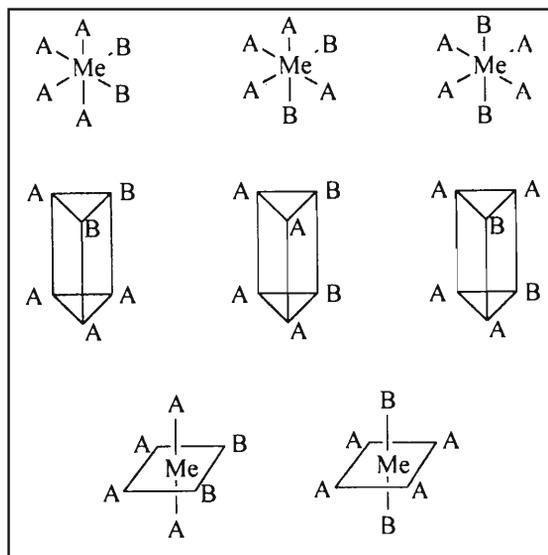
involved: (1) plane, (2) prismatic, (3) octahedron (Figure 1). Plane and prismatic arrangements require, for compounds with complex radicals $[\text{MeA}_4\text{B}_2]$, the occurrence of three isomeric forms, whereas the octahedron arrangement only envisages the existence of two isomeric compounds of this nature (Figure 2). The latter isomers are characterized in that one form contains the two B groups in the 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 ($[\text{MeA}_4\text{B}_2]$) do in fact occur in two isomeric forms; in no case were three isomeric forms found to exist (see Figure 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.

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

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: $[\text{MeA}_5\text{B}]$. Of symmetrical arrangements, the following may be

Figure 2.



mirror-image isomers. In this lecture I shall merely discuss briefly a few cases which have been confirmed by experimental investigations. 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

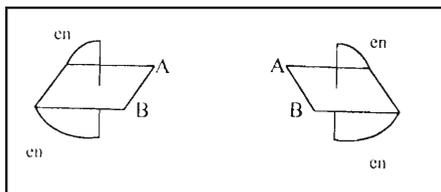


Figure 3.

constructions become possible whose relationship to one another is that of two mirror-image forms which cannot be superimposed on each other (Figure 3). Compounds which satisfy these conditions include the following: $[\text{CoClNH}_3\text{en}_2]\text{X}_2$, $[\text{CoBrNH}_3\text{en}_2]\text{X}_2$. 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 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: $[\text{CoA}_2\text{en}_2]$, with two A groups in adjacent positions. Even in this case, image and mirror image cannot be superimposed (Figure 4). It was therefore of great interest to examine whether optical 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: $[\text{CoCl}_2\text{en}_2]\text{X}$, $[\text{CrCl}_2\text{en}_2]\text{X}$. Further, we were able to resolve the *cis*-dinitro-diethylenediamine cobalt

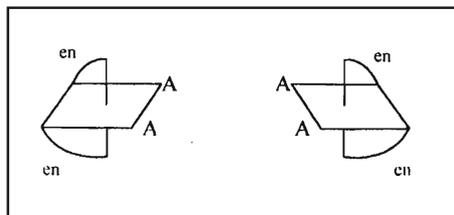


Figure 4.

salts and the *cis*-diamine-diethylenediamine cobalt salts into the active forms, and the active carbonato- 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

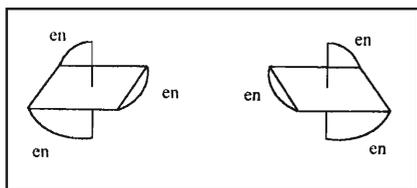


Figure 5.

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 (Figure 5). 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: $[\text{Coen}_3]\text{X}_3$, $[\text{Cren}_3]\text{X}_3$, $[\text{Rhen}_3]\text{X}_3$, for iron, the tri- α -dipyridyl compounds: $[\text{FeDpy}_3]\text{X}_2$. 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: $[\text{Co}(\text{C}_2\text{O}_4)_3]\text{R}_3$, $[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{R}_3$, $[\text{Rh}(\text{C}_2\text{O}_4)_3]\text{R}_3$.

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.



In accepting an honorary degree from the University of Notre Dame a few years ago, General David Sarnoff [head of RCA] made this statement: "We are too prone to make technological instruments the scapegoats for the sins of those who wield them. The products of modern science are not in themselves good or bad; it is the way they are used that determines their value." That is the voice of the current somnambulism. Suppose we were to say, "Apple pie is in itself neither good nor bad; it is the way it is used that determines its value." ... There is nothing in the Sarnoff statement that will bear scrutiny, for it ignores the nature of the medium, of any and all media, in the true Narcissus style of one hypnotized by the amputation and extension of his own being in a new technical form... It has never occurred to General Sarnoff that any technology could do anything but-add-itself on to what we already are.

Marshall McLuhan