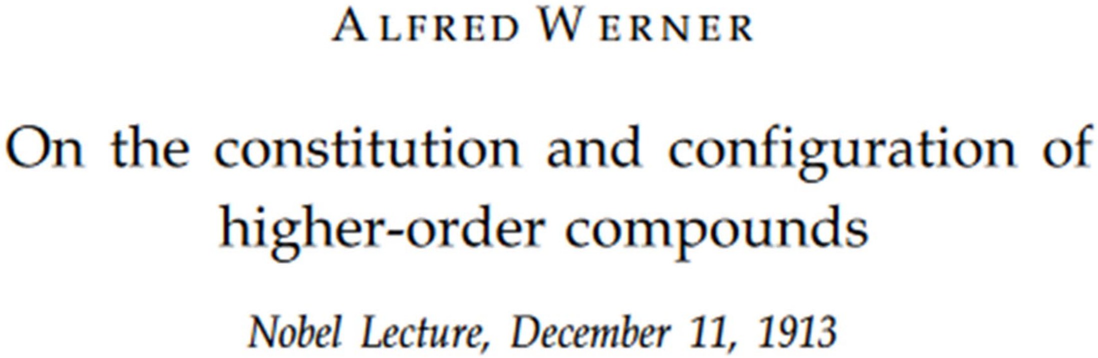
Classic Paper



ALFRED WERNER

On the constitution and configuration of higher-order compounds

Nobel Lecture, December 11, 1913

Riya Dutta
6.01.24

Alfred Werner: the well-coordinated chemist

Photo from the Nobel Foundation archive.

Alfred Werner

Prize share: 1/1

The Nobel Prize in Chemistry 1913 was awarded to Alfred Werner "in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry"

First Inorganic Nobel Prize Laureate

Most previous Nobel chemistry awards had been won by organic chemists like Emil Fischer (1902) or physical chemists like Wilhelm Ostwald (1909). Two chemistry prizes even went to physicists – Ernest Rutherford (1908) and Marie Curie (1911).

So in 1913 it was no surprise that inorganic chemistry's turn had come.

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ALFRED WERNER

On the constitution and configuration of higher-order compounds

Nobel Lecture, December 11, 1913

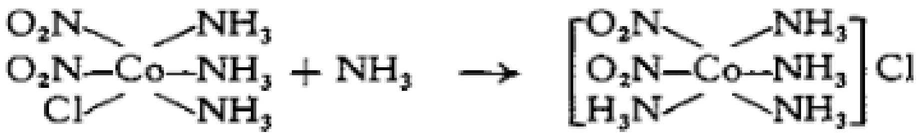
Allow me first of all to express my deeply felt gratitude to the Swedish Academy of Sciences for the distinction granted to me and for the honour of being invited to present to you an account of the progress of our knowledge concerning the structure of the molecules.

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

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:

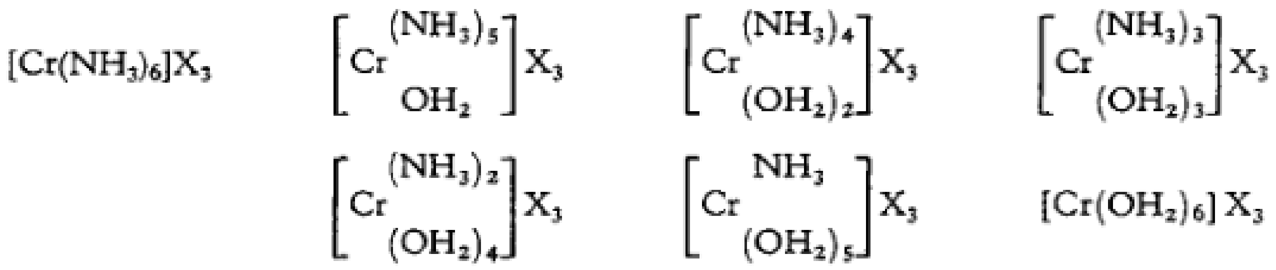
The addition compounds are joined by a second group of higher-order compounds, i.e. the intercalation compounds. These form when, as a result of the incorporation of a new component, the acid residues of a compound are displaced from the direct bond with the metal atom. The following is an example:



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:

$$[\mathrm{Me}(\mathrm{NH}_3)_6]\mathrm{X}_n$$

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:



$$[\mathrm{Cr}(\mathrm{NH}_3)_6]\mathrm{X}_3 \qquad \left[\mathrm{Cr}\begin{matrix}(\mathrm{NH}_3)_5\\ \mathrm{OH}_2\end{matrix}\right]\mathrm{X}_3 \qquad \left[\mathrm{Cr}\begin{matrix}(\mathrm{NH}_3)_4\\ (\mathrm{OH}_2)_2\end{matrix}\right]\mathrm{X}_3 \qquad \left[\mathrm{Cr}\begin{matrix}(\mathrm{NH}_3)_3\\ (\mathrm{OH}_2)_3\end{matrix}\right]\mathrm{X}_3$$

$$\left[\mathrm{Cr}\begin{matrix}(\mathrm{NH}_3)_2\\ (\mathrm{OH}_2)_4\end{matrix}\right]\mathrm{X}_3 \qquad \left[\mathrm{Cr}\begin{matrix}\mathrm{NH}_3\\ (\mathrm{OH}_2)_5\end{matrix}\right]\mathrm{X}_3 \qquad [\mathrm{Cr}(\mathrm{OH}_2)_6]\mathrm{X}_3$$

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 : $[\mathrm{Me}^{A_5}_{B}]$. Of symmetrical arrangements, the following may be involved : (I) plane, (2) prismatic, (3) octahedron (Fig.I).

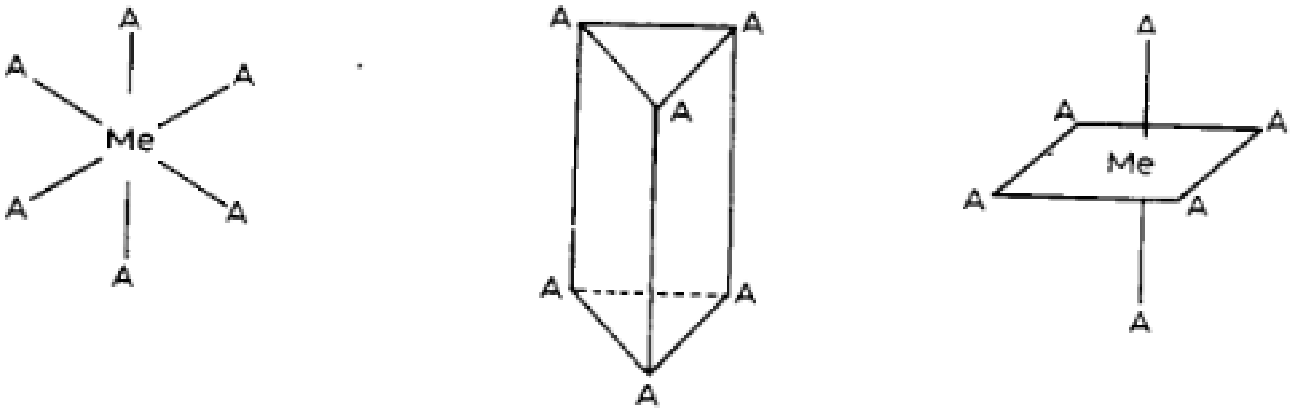


Fig. 1.

Plane and prismatic arrangements require, for compounds with complex radicals $[\mathrm{Me}^{B_2}_{A_4}]$, 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 $[\mathrm{Me}^{B_2}_{A_4}]$ do in fact occur in two isomeric forms; in no case were

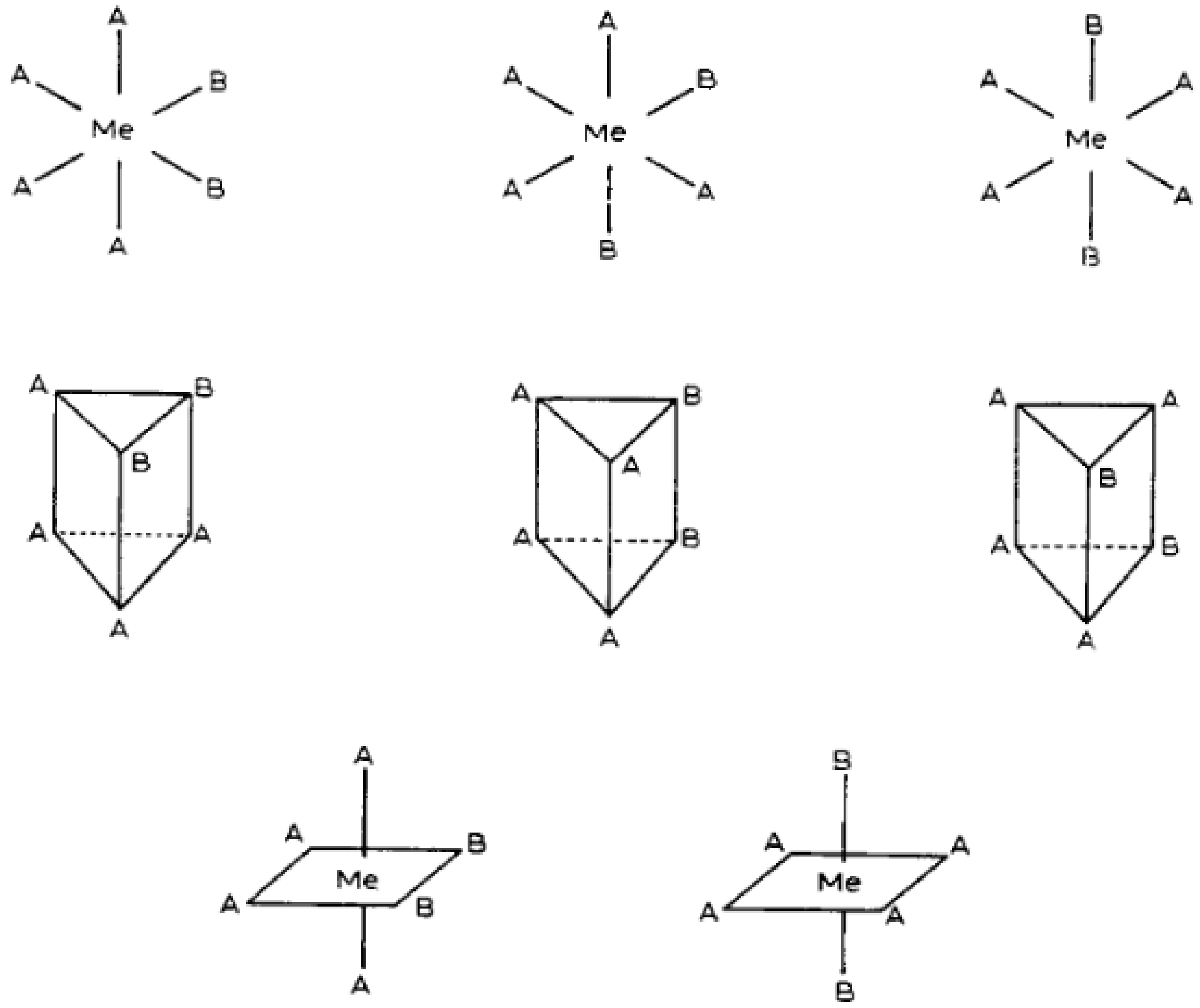

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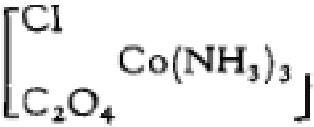
Fig.2.

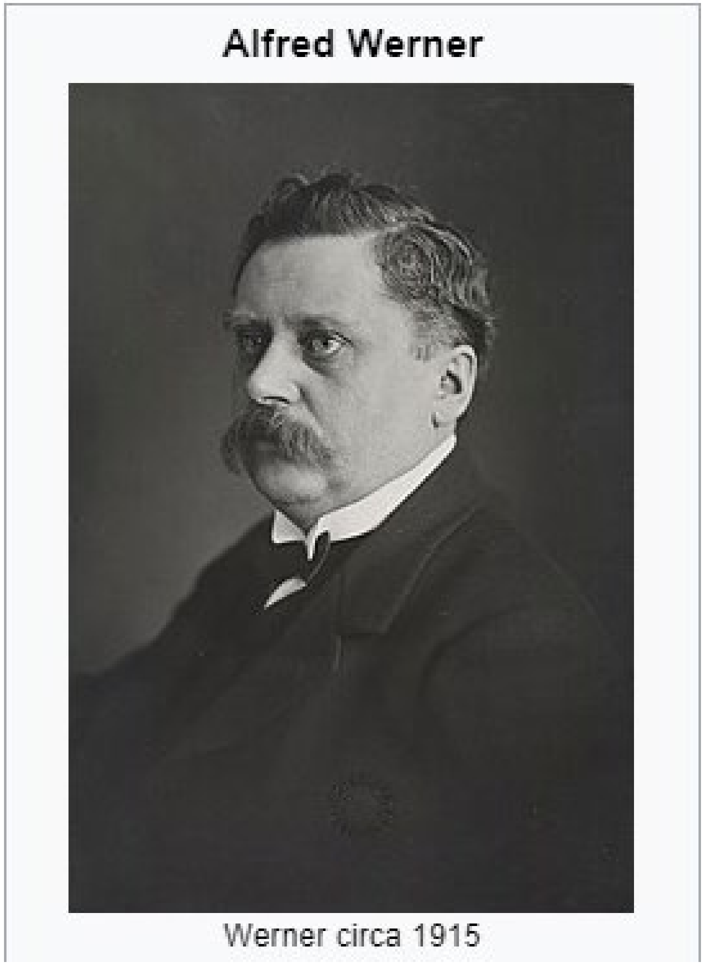
This conclusion also has recently been confirmed. The compound:



$$\left[\begin{matrix}\mathrm{Cl}\\ \mathrm{C_2O_4}\end{matrix}\mathrm{Co(NH_3)_3}\right]$$

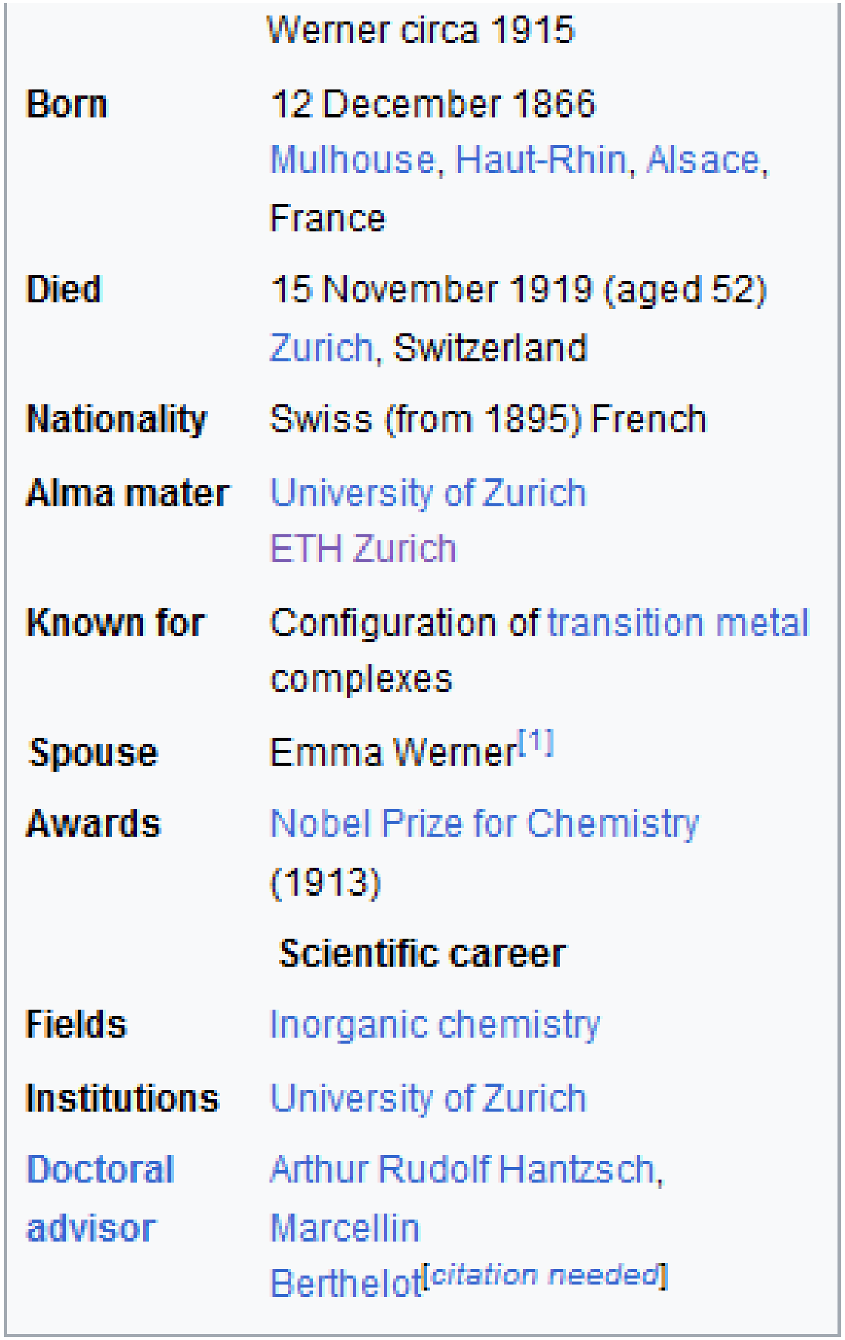
for example, exists in two isomeric forms, of which one is indigo blue and the other violet. With respect to the phenomena of the so-called geometrical stereo-isomerism, all the conclusions drawn from theory have been confirmed in such a perfect manner that there can be no further doubt as to the correctness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



Alfred Werner

Werner circa 1915



Werner circa 1915

Born	12 December 1866 Mulhouse, Haut-Rhin, Alsace, France
Died	15 November 1919 (aged 52) Zurich, Switzerland
Nationality	Swiss (from 1895) French
Alma mater	University of Zurich ETH Zurich
Known for	Configuration of transition metal complexes
Spouse	Emma Werner[1]
Awards	Nobel Prize for Chemistry (1913)
	Scientific career
Fields	Inorganic chemistry
Institutions	University of Zurich
Doctoral advisor	Arthur Rudolf Hantzsch, Marcellin Berthelot[*citation needed*]

Thank You