

# Old and New ‘Anschauungen in der Anorganischen Chemie’ A Homage to Alfred Werner’s Book and Intuition

## Part I. Alfred Werner’s Book and Coordination Theory

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**Abstract:** Alfred Werner (1866–1919) is regarded as the founder of coordination chemistry. He was the author of the book entitled ‘Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie’ (New Perspectives in Inorganic Chemistry) which guided generations of chemists in research and teaching. This book was recently awarded the ‘Citation for Chemical Breakthrough’ prize from the Division of the History of Chemistry of the American Chemical Society. This article is the first of three dedicated to Werner’s life and works.

**Keywords:** Coordination theory · History of Chemistry · Werner, A.

### Preface

Alfred Werner (1866–1919) was a chemist of great intuitive capability. Based on this ability and his great chemistry accomplishments at the University of Zurich, he is regarded as the founder of coordination chemistry. Alfred Werner wrote a book on coordination chemistry, which not only comprised the state of the art, but also its conceptual background during the years of 1900 to 1920. This book guided generations of chemists in research and teaching and thus gained enormous importance for the chemistry developments. Therefore this book was recently awarded the ‘Citation for Chemical Breakthrough’ prize from the Division of the History of Chemistry of the American Chemical Society [http://www.scs.uiuc.edu/~mainzv/HIST/awards/citations\\_chem-breakthroughs.php](http://www.scs.uiuc.edu/~mainzv/HIST/awards/citations_chem-breakthroughs.php). In appreciation of this honour and in allusion to Werner’s book this personal account of the author was created. It will appear in three parts: Part I reviews Alfred Werner’s book and coordination theory; Parts II and III will give examples of Alfred Werner’s intuition by aid of contemporary studies of complexes from the Werner Collection of original samples of the University of Zurich.

### Werner’s book and the ‘Citation for Chemical Breakthrough’ Award of the American Chemical Society

At the occasion of the yearly Symposium of the Chemical Society of Zurich, December 3, 2009, the Division of History of Chemistry of the American Chemical Society honored the Fachbereich Chemie of the University of Zurich with the plaque

#### ‘Citation for Chemical Breakthrough’

to commemorate the outstanding achievement of Alfred Werner’s book (Fig. 1):

#### ‘Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie’

Alfred Werner’s outstanding contributions to coordination chemistry were also honored with the Nobel Prize<sup>[1]</sup> and numerous biographical reviews<sup>[2]</sup> and articles on Alfred Werner’s coordination chemistry,<sup>[3]</sup> which paid adequate credit to the great achievements of the “founder of coordination chemistry”. The plaque praises the book’s main theme, which is a chemical concept:

*“The concept of coordination compounds: How ions and groups of atoms bind and arrange around a central metal atom in three dimensions”*

Early concepts of chemistry did not normally survive for a period of over 100 years, as they adopted progress in the field and were thus often subjected to changes. It would be quite arrogant and presumptu-

ous to claim that Alfred Werner’s concepts of coordination chemistry have reached eternal validity. Certainly quite a few aspects did survive, and others only in parts. In conjunction with this the quite stringent question can be posed of what has remained valid from his ‘Anschauungen’. This article in three parts will try to find an answer to this question. At the moment we can say that there are only very few concepts of early modern times chemistry, meaning of those of the 19th century, which have survived to the same extent as Alfred Werner’s concepts. This article will therefore try to review his concept and put them into the perspective of the present times. Alfred Werner’s approach to coordination chemistry was actually one of the first conceptual approaches of chemistry, where ‘theory’ came to some extent before ‘experiment’. As we will see later Alfred Werner’s ‘theory’ was laid down as early as 1893, so really at the beginning of his work in coordination chemistry. Alfred Werner’s book is the expression of Alfred Werner’s conceptual imagination and just from this point of view, it indeed deserves the consideration, the awareness, given by the American Chemical Society with this award.

But Alfred Werner’s book should be acknowledged in other respects, since it had great impact on 100 years of developments in chemistry. His ‘Anschauungen’ were the foundation for progress in coordination chemistry research and its branching out into adjacent areas and became thus also a base for the interdisciplinary developments of this field.

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Fig. 1. Left: Picture of Alfred Werner's book 'Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie', which appeared in the series 'Die Wissenschaft. Einzeldarstellungen aus der Natur, Wissenschaft und Technik', Friedrich Vieweg & Sohn, Braunschweig: First edition 1905, 2nd edition 1909, 3rd edition 1913, 4th edition 1920, 5th edition 1923. The 5th edition appeared after Werner's death and was edited by Professor P. Pfeiffer, University of Bonn, Germany (Professor P. Pfeiffer was a 'Dozent' at the Chemisches Institut of the University of Zurich, later professor of chemistry at the University of Bonn). Right: Picture featuring the presentation of the plaque award of the Division of History of the American Chemical Society (HIST). Professor H. Berke, receiving the plaque in the name of the Fachbereich Chemie of the University of Zurich (left) and Professor D. Arigoni, ETH Zürich, American Chemical Society delegate handing the plaque over (right).

Immediately after the book's first appearance in 1905 and 12 years after Alfred Werner's legendary publication on coordination theory, Alfred Werner's book advanced to the main guide in the field of coordination chemistry. It was supplemented in four more editions maturing through the years till 1923. In this period of time, this book not only functioned as a compendium with comprehensive coverage of descriptive phenomenological coordination chemistry, but indeed also documented the state of the art of the theoretical and conceptual knowledge in the field. Needless to say at the time the leading views were those of Alfred Werner, putting coordination chemistry on solid ground. Alfred Werner's input was so enormous in quantity and quality that it has retained validity even a hundred years later. It still can be considered a proper base for research and teaching in schools and academics. The University of Zurich is proud to once have hosted Alfred Werner and to have been the place that provided him opportunity to lay the foundations of coordination chemistry. Alfred Werner's book is to a great extent a personal account overviewing his and his research group's achievements in the field. In this article we will review excerpts from his book. We do not attempt to be comprehensive in tracing the basis for today's coordination chemistry and its extension into other areas; rather we would like to go back to the roots of Alfred Werner's chemistry in a more per-

sonal and amusing way, finding the anecdotal origins of some ideas that have modern implications and applications.

Over the years the author has investigated, or more accurately, has reinvestigated some of the original samples of the Werner group compiled in the collection of original samples at the University of Zurich. The main impetus for this came from the idea to create an impression of Alfred Werner's intuition. Intuition is based on imagination, inspiration and knowledge and according to Werner's contemporary Albert Einstein, imagination is more important than knowledge. Alfred Werner's book indeed witnesses in a unique way comprehensive knowledge of the turn of the century. With Einstein's correct assessment in mind we feel it too boring to survey a time's knowledge; rather we would like to trace Werner's imaginative abilities and how his inspirations came about *via* selective insights into his developments in coordination chemistry.

Before we start a deeper 'analysis' of Alfred Werner's intuition and inspiration on the basis of accounts of his work deposited in the form of original samples, we would like to briefly review his life and his views of coordination chemistry.

### Short Survey of Alfred Alfred Werner's Life

Werner's short but intense life<sup>[2]</sup> was dedicated mainly to chemistry. His devotion to chemistry started with first inspirations

in the subject in Mulhouse guided by his school teacher. His main chemistry endeavors started with his enrollment as student at the ETH Zürich in 1887. He then made a PhD thesis with Professor Hantzsch, a pioneering pyridine chemist. After he received the 'call' to the University of Zurich as an associate professor in 1893 he made contact with Professor A. Miolati from Turin, from whom he learned to carry out conductivity measurements, which in its essence is a very effective analytical tool for 'counting' ions of complexes in solution helping greatly to unravel their 'constitution' of complexes. His inspiration for the 'Constitution of Inorganic Compounds' (complexes) came suddenly as a 'flash of genius' in late 1892. The following is reported:

For one night in late 1892 Alfred Werner awoke at 2 a.m. with the solution of the constitution of 'molecular compounds', which had come to him like a flash of lightning. He arose from his bed and wrote furiously and without interruption. By 5 p.m. of the following day he had finished his most famous paper titled: 'Contribution to the Constitution of Inorganic Compounds', A. Werner, *Zeitschrift für Anorganische Chemie* **1893**, 2, 267.

He was already full professor at the time when the first edition of his book appeared in 1905. His chemistry endeavors reached a first peak in the understanding of complexes as stereochemical three-dimensional molecules possessing a special binding mode different from those of organic chemistry. A great event and maybe also another inspirational push to his research came when he and his group moved to the new chemistry building in Rämistrasse in 1909, which celebrates its centennial this year. This move apparently gave support to another peak of scientific achievement: the discovery of the chirality of complexes. The first optical resolution of complexes was carried out in 1911 by his American coworker V. L. King and the first chiral separation of a non-carbon containing purely inorganic complex was accomplished in 1913 by Alfred Werner's coworker C. Schwenk. 1913 was a good year for Alfred Werner, since he was also awarded the Nobel Prize<sup>[1]</sup> and his coordination chemistry became broadly accepted. Despite this broad acceptance, and even a personal visit on his return trip from Stockholm, Alfred Werner was never able to reconcile with his chief scientific adversary Jørgensen (University of Copenhagen). Not too long after Alfred Werner fell ill, with continuous physical and mental decline from 1915 till his death in 1919.

### Alfred Werner's Scientific Life

1866 Born in Mulhouse  
1887 Enrollment as a student of chemistry at the ETH Zürich



Fig. 2. Alfred Werner.

- 1889 Diploma of Chemistry, ETH Zürich
- 1890 PhD with Prof. Hantzsch at ETH Zürich
- 1892 Habilitation ETH Zürich, unsalaried Privatdozent
- 1892 Werner met Prof. A. Miolati
- 1893 Associate Professor, University of Zurich
- 1893 Coordination theory
- 1895 Full Professor, University of Zurich
- 1895 Marriage and Swiss nationality
- 1905 Book 'Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie'
- 1909 New chemistry building
- 1910 Discovery of the chirality of complexes by coworker V. L. King
- 1913 Discovery of inorganic non-carbon containing chiral complexes by coworker C. Schwenk
- 1913 Nobel Prize
- 1915 Descent into illness
- 1919 Death

### Alfred Werner's Views of Coordination Chemistry as Documented in Werner's Book

Alfred Werner revolutionized the world of coordination compounds by stating a new set of stereochemical and bonding principles.<sup>[1-3]</sup> He proved the Blomstrand-Jørgensen concept of coordination chemistry wrong, which restricted itself to two-dimensional 'flat' views of coordination compounds and gave rise to a great deal of conceptual inconsistency. Giving complexes a third dimension provided correct explanations for their inherent principles of isomerism including those originating from chirality. The different ways of explaining positional isomerism within the

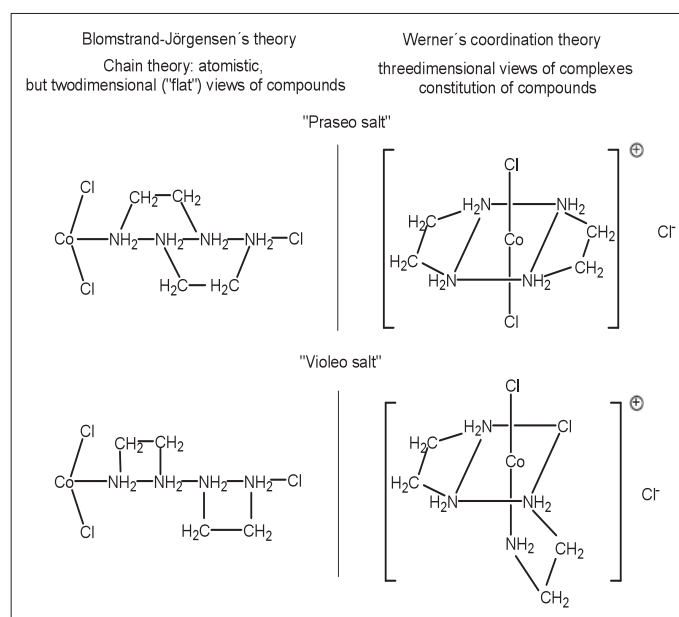


Fig. 3. Positional isomerism in praseo and violeo salts as interpreted by Blomstrand-Jørgensen and Werner.

Blomstrand-Jørgensen concept and Alfred Werner's theory is exemplified in Fig. 3 with the praseo and the violeo salts.

Concomitant with these stereochemical views, Alfred Werner put forward a new concept of bonding in complexes, which he denoted as 'higher order compounds'. The higher order was derived from the apparently inevitable distinction between a primary (Hauptvalenz) and a secondary valency (Nebenvaleanz). In his terminology the primary valency caused 'inclusion' complexes ('Einlagerungsverbindungen'), which would in modern terms be attributed a metal-ligand bonding mode based formally on radicals allowing formulation of a covalent interaction. As an additional feature of this primary valency, Alfred Werner realized that these radical derived bonds are made in complexes from ligand species stable as anions in the free state. These anions can thus be replaced by neutral ligands without destruction of the primary valency or exchange of it into a secondary one. Primary valency in complexes is thus expressed and can be counted by overall charges on the complex and the number of anionic ligands. To illustrate this we would like to analyze the equations in Fig. 4, taken directly from Werner's book (3rd ed., p. 46).

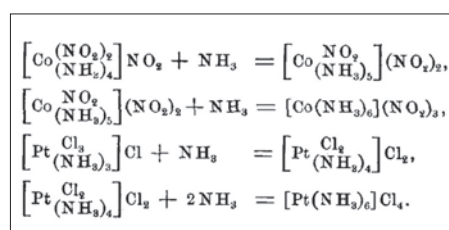


Fig. 4. Equations taken from Werner's book, 3rd ed., p. 46.

The anionic ligands (Co-NO<sub>2</sub> or Pt-Cl) can be replaced with neutral ligands (Co-NH<sub>3</sub><sup>+</sup> or Pt-NH<sub>3</sub><sup>+</sup>) without loss of primary valency. The primary valency corresponds to a saturation of charges in the complexes; in certain cases the demand for ionic saturation cannot be satisfied, leaving charge behind, although the compounds still possess some ligands bound through primary valency.

It can be speculated that the formulation of this primary valency as a binding category of its own had to do with Alfred Werner's primary experience in conductivity measurements (initially together with Professor A. Miolati from Turin). The replacement of ionic ligands by neutral ones allows series of complexes to be established with different charges, but with a stable number of primary valencies. Fig. 5 demonstrates such a series and their conductivities.

Secondary valency was meant to give rise to addition compounds ('Anlagerungsverbindung'), which in more modern binding terms could be described as Lewis acid-base interactions. Typical interactions of secondary valency were described in Alfred Werner's book, for instance for metal carbonyls (Fig. 6).

This excerpt from his book (3rd ed., p. 303) witnesses not only the book's actuality, but also the correct view of binding of CO to a metal center to form 'addition' compounds. It should be noted at this point that the cited discoverers of metal carbonyls Mond and Langer described incorrectly the 'constitution' of metal carbonyls. First of all in their view these were 'flat' molecules closer in their representation to the Blomstrand-Jørgensen theory,<sup>[2]</sup> and secondly in Alfred Werner's terminology they would have been 'inclusion' compounds.



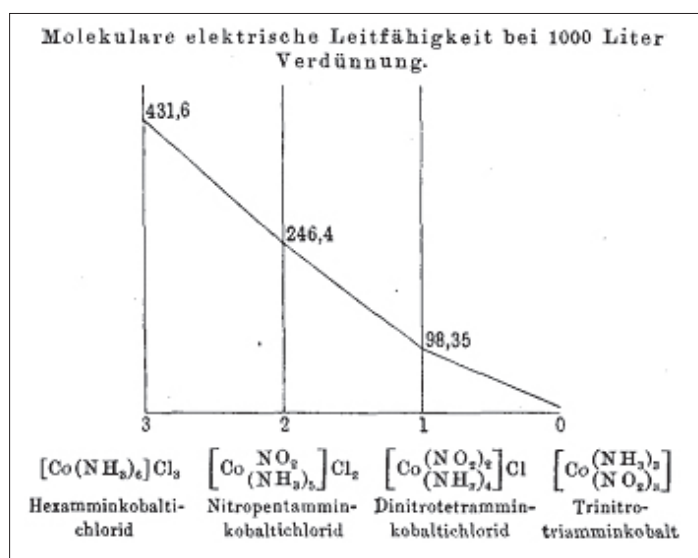


Fig. 5. Conductivities for the complex series  $[\text{Co}(\text{NH}_3)_{6-n}(\text{NO}_2)_n]\text{Cl}_{3-n}$  ( $n = 0 - 3$ ). Plot taken from Werner's book (3rd ed., p. 46).

Koordinationsverbindungen mit Komponenten in zweiter Sphäre. 303

Recht interessante Nebenvalenzverbindungen von Metallen sind die Kohlenoxydverbindungen. Daß sich das Kohlenoxyd in seinen Additionsverbindungen mit Schwermetallen in Nebenvalenzbindung befindet, ergibt sich aus dem Verhalten des Carbonylferrocyanalkaliums und der Kohlenoxydverbindungen des Platinchlorids. Man kennt heute folgende Metallcarbonylverbindungen:

$\text{Fe}(\text{CO})_5^1$ , bernsteingelbe Flüssigkeit	$\text{Fe}_2(\text{CO})_9$ , goldfarbige Kristalle
$\text{Co}(\text{CO})_4^2$ , schwarze Kristalle (kryoskopisch bimolekular)	$\text{Ni}(\text{CO})_4^3$ , farblose Flüssigkeit
$\text{Mo}(\text{CO})_6^2$ , weiße Kristalle (leicht sublimierend)	$\text{Ru}(\text{CO})_x^3$ , orangefarbige Kristalle

<sup>1</sup>) L. Mond und Langer, Chem. News **64**, 294 (1891). —  
<sup>2</sup>) L. Mond, H. Hirtz und M. D. Cowap, Zeitschr. f. anorg. Chem. **68**, 207 (1910). — <sup>3</sup>) L. Mond, Langer und Anincke, Chem. News **62**, 97 (1890); M. Berthelot, Compt. rend. **112**, 1343 (1891).

Die Konstitution dieser Verbindungen ist im Sinne folgender Formeln aufzufassen:

OC . CO	OC . CO	OC . CO
OC · Mo · CO,	Fe · CO,	Ni ·
OC · CO	OC · CO	OC · CO

Fig. 6. Excerpt from Werner's book (3rd ed., p. 303) describing secondary valencies in carbonyl compounds.

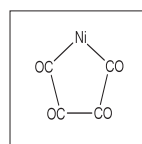


Fig. 7. Mond/Langer description of nickel carbonyl

Nickel carbonyl,  $\text{Ni}(\text{CO})_4$ , thus featured in the Mond and Langer representation as a cyclic organic molecule (Fig. 7).

Within the concept of primary and secondary valencies, Alfred Werner applied the term affinity. Affinities presumably meant in this context binding strength in complexes, which allowed qualitative modification of these valencies. The listing below summarizes Werner's binding concept:

– Inclusion compounds (Einlagerungsverbindungen) based on primary valency, describes binding of ionic units and replacement of ionic units by neutral units leaving charges

– Addition compounds (Anlagerungsverbindungen) are based on secondary valency, which are coordinative bound

– Affinity theory, corresponds to a 'qualitative' quantification of binding strength in complexes

To conclude this overview of Werner's book and theory, it must first of all be said that a great deal Werner's theory has to be considered heuristic: when applied to complexes it worked well, but in great parts it seemed somewhat diffuse. In modern terms the diffuseness came from the fact that his picture was not electronically based, unlike Lewis's theory. This was the main criticism of P. Pfeiffer, who therefore changed the chapter on binding theory in the last edition of Werner's book. In the preface to this edition P. Pfeiffer wrote that Werner's theoretical concept should

be replaced by Kossel's theory of 1916, which was very similar to Lewis' theory of 1923. Indeed the Kossel/Lewis theory brought about more unifying electronic views on valency in general and on that of complexes in particular.

## Werner's Intuition

As we said intuition is based on imagination, inspiration and knowledge. We have already seen where Werner's inspirational moments could have had their origins in his life. We next would like to approach Werner's intuition. Since scientific intuition needs concepts, and we surveyed his concepts concerning coordination theory, so that we would now be able to trace Werner's intuition by contemporary studies of the Werner Collection of Samples, which will be described in the form of anecdotes in Part II and III of this series.

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