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Alfred Werner: A Forerunner to Modern Inorganic Chemistry

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chirality · coordination modes · history of chemistry · Werner, Alfred

In memory of Franz Hein

"Alfred Werner, whose 100th birthday we celebrate this year, was a star of unequaled brilliance in Europe's intellectual firmament. Coming from a humble background, this hero in mind attained in the life span of fifty years a brilliance, which will continue to shine for centuries. Alfred Werner passed away physically, but making full use of his ideas will be a task for generations."

This quotation from 1966 does not stem from a former co-worker of Werner's or a coordination chemist of a later generation, but from Leopold Horner, an eminent organic chemist, who carried out pioneering studies on the stereochemistry of compounds of the Group 15 elements of the periodic table, in particular phosphorus and arsenic, in the second half of the 20th century.[1] The great respect expressed in these words, which was shared by numerous other organic chemists, was not only due to the fact that at the beginning of his career Werner was undecided whether he should focus on inorganic or organic chemistry,[2] but made clear that Werner's work was of great significance far beyond a single field of chemistry, and remains so today.[3,4]

Figure 1. Alfred Werner (1866–1919), a pioneer of modern inorganic chemistry [photograph and citation from *Angew. Chem.* **1966**, *78*, 1069].

Alfred Werner (Figure 1) was born on December 12, 1866 in Mulhouse in Alsace, a town which from 1870/71 (after the end of the Franco–Prussian War) until 1918 was part of Germany and referred to as Mülhausen.[5] He discoverd a particular passion for chemistry already at school and installed a small makeshift lab in a barn on his father's farm. From 1878 to 1885 he attended the Höhere Gewerbeschule (École Professionelle) in his hometown, which further deepened his interest in chemistry. After supplementing his pocket money through occasional services for friends, he bought several chemistry textbooks and at the age of 18 he presented his first manuscript to Professor Emilio Noelting, the Director of the Chemieschule in Mulhouse. As Paul Karrer, his co-worker in later years reported,[6] he asked Noelting "how long it took roughly to become a professor". Apparently, the evasive answer did not curb Werner's enthusiasm, since he used his free time during his military service as a "one-year volunteer" (beginning on October 1, 1885) at Karlsruhe to attend some chemistry lectures held by Carl Engler at the Großherzogliche Technische Hochschule (now Karlsruhe Institute of Technology, KIT).

One year later, Werner moved from Karlsruhe to Zurich, where he began his studies in chemistry in the winter semester 1886/87 at the Eidgenössisches Polytechnikum (nowadays ETH). The reason to choose the "Poly" and not the University of Zurich, which was more prestigious in those days, was that the Polytechnikum was the only institution of university standard in Europe that accepted students without an *Abiturabschluss* (maturity certificate), provided they the passed the obligatory entrance examination.[7] Werner passed the exam with distinction having minor difficulties only in mathematics.[6,8] Already in 1889 he completed his Diploma thesis under the supervision of Georg Lunge and Arthur Hantzsch; he stayed in Lunge's chemical-technical laboratory as a teaching assistent, but worked at the same time on his PhD thesis with Arthur Hantzsch (Figure 2).[9,10] He submitted his thesis at the University of Zurich, because the Polytechnikum did not receive the "ius promovendi" (authorization to grant PhD titles) until 1909.[11] Werner's thesis entitled "Über die räumliche Anordnung der Atome in stickstoffhaltigen Verbindungen" was reviewed by Viktor Merz and Haruthiun Abeljanz, who both had chairs at the University of Zurich, and they approved the work as "sehr günstig" (very favorable). The *Clausurarbeit* (final paper) "Über die Theorie der aromatischen Verbindungen" equally received the grade "ganz ausgezeichnet" (quite outstanding).[11] On October 13, 1890 Werner was awarded the degree

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Figure 2. Alfred Werner (left) and Arthur Hantzsch in 1910 (photograph from Ref. [12]).[13]

Dr. phil. "unter besonderer Anerkennung vorzüglicher Leistung" (with special recognition of superior performance).

After passing the PhD examination, Werner followed Hantzsch's advice and went to Marcellin Berthelot at the Collège de France in Paris for several months. The funding for this visit was generously provided by his former supervisor Georg Lunge.[14] Back at Zurich Werner began working on his *Habilitationsschrift*, in which he described the results of his independent research. On October 16, 1891 he submitted the Habilitation thesis to the Hohe Schweizerische Schulrat and added the petition to award him the "venia docendi" (authorization to lecture) at the Polytechnikum.[15] The first and major part of the *Habilitationsschrift* entitled "Beiträge zur Theorie der Affinität und Valenz" was no less than an attack on Kekulé's concept of rigid directed valences of atoms. In contrast to Kekulé, the "supreme patriarch of structural organic chemistry",[16] Werner offered a more flexible approach described on page 9 of his *Habilitationsschrift* as follows: "The affinity is an attracting force, directed equally from the center of an atom to all parts of the sphere. According to this view, the necessary conclusion is that directed valence units don't exist. The term valence represents an independent, empirically found numerical ratio, in which the atoms are connected to each other". And he added as subscript: "That the proposal of valence units serves to explain the numerical ratio, in which the atoms are bound to each other, is in fact not an explanation but a rephrasing of the idea itself."[17] The second and the experimental part of the *Habilitationsschrift* was entitled "Über die Stereochemie des Stickstoffs in der Benzhydroxamsäurereihe" and was published separately by Werner in 1892 and 1893.[18]

Helmut Werner studied chemistry in Jena and Munich and received his PhD with E. O. Fischer in 1961. After postdoctoral work with J. H. Richards at Caltech he became Professor of Inorganic Chemistry at the University of Zürich and was appointed Professor and Head of the Institute of Inorganic Chemistry at the University of Würzburg in 1975. He has been Professor Emeritus since 2002. Apart from numerous international awards he received the prestigious Alfred Stock Prize of the German Chemical Society in 1988 and was elected as a member of the Academy Leopoldina (now: National Academy of Sciences) in the same year. He received honorary doctorates from the University of Zaragoza (2001) and from the University of Jena (2006).

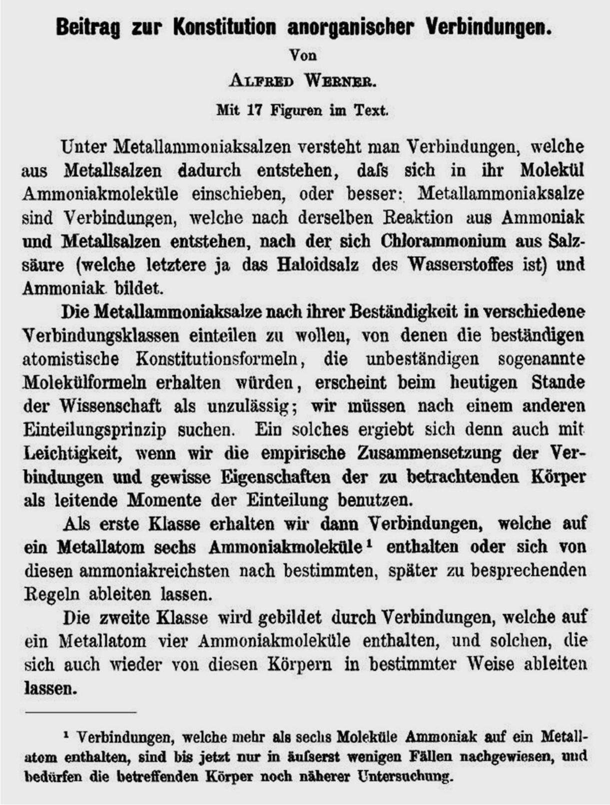
In his evaluation Hantzsch praised the content of the *Habilitationsschrift* and merely pointed out some descriptive and grammatical errors, which he found excusable owing to Werner's Alsatian background. In contrast, he emphasized the "extraordinary originality" and the "clear and comprehensive expression" of Werner's ideas. He concluded that "the *Habilitationsschrift* of Dr. Werner may be judged as not only a good, but an excellent scientific achievement" which will be appreciated in "wider chemical circles".[19] Werner published the theoretical part of the *Habilitationsschrift* in the *Vierteljahrsschrift der Naturforschenden Gesellschaft in Zürich*, which was a journal of limited circulation with the effect that the work remained almost unnoticed.[19]

Based on Hantzsch's review the *Hohe Schweizerische Schulrat* accepted the *Habilitationsschrift* and appointed Alfred Werner on January 4, 1892 to the position of Privat-Dozent in der Freifächerabtheilung (elective subjects division) of the *Polytechnikum*.[20] In the next three semesters (from summer 1892 until summer 1893) Werner lectured on "Atomic Theory", "Selected Topics in Inorganic Chemistry", "Comparative Organic Chemistry" and "Stereochemistry", and announced that in the winter semester 1893/94 he intended to repeat his lecture on "Selected Topics in Inorganic Chemistry" and also to teach a course on "The Chemistry of Naphthalene, Anthracene and Higher Ring Compounds".[11] However, these courses were never given because in August 1893 Werner received a call to the University of Zurich which he accepted soon thereafter.

Before the offer was made, the faculty committee also considered two other scientists as suitable candidates for the vacant position, namely Associate Professor Hans von Pechmann and Associate Professor F. K. J. Thiele (both from the University of Munich). The experts Adolf von Bayer, Emil Fischer, and Arthur Hantzsch ranked von Pechmann and Werner as equal, but both better than Thiele, which raised some eyebrows.[11] After the members of the appointment committee attended one of Werner's courses and also his lecture at the Naturforschende Gesellschaft in Zürich, they decided in his favor. Thus, on September 29, 1893 the government of the canton of Zurich appointed Werner as Extraordinarius (associate professor) for the usual term of six years. As the successor to Viktor Merz he was obliged to head in the Chemische Universitätsinstitut the Laboratorium A, which was in charge of students majoring in chemistry. The Laboratorium B, serving students in medicine and nutritional chemistry as well as teaching candidates, was headed by Professor Haruthiun Abeljanz, who had already taught at the University of Zurich for 20 years and was 17 years senior to Werner. Quite soon, an unpleasant conflict developed between the two scientists, mainly because Werner was permitted to hold only the main lecture in organic but not in inorganic chemistry.[21] The continuing confrontation is described in detail by George B. Kauffman in his extensive monograph, which also states that this internal conflict harmed Werner internationally more than he deserved.[22]

It is worth briefly commenting on the above-mentioned excitement[11] concerning the decision in favor of Werner. The faculty committee was undoubtedly aware that of the three candidates considered to succeed Viktor Merz, in particular Hans von Pechmann (1850–1902) was not only senior and more experienced but in contrast to Werner already well known in the chemical community. However, some members of the committee were afraid that in view of the offered salary, which was hardly generous, Hans von Pechmann would decide to stay at Munich and prefer a call to a German university.[23] Moreover, the existing conditions of the laboratories belonging to the Laboratorium A of the Chemische Universitätsinstitut were "extremely primitive and inconvenient, … the doctoral students were housed in unfinished cellars and wooden sheds, in which artificial gas lightening was required even at noon. … The cold cement floors along with the poor heating and the inadequate steam pipes overhead made those rooms extremely unhealthy. They aptly deserved the nickname 'catacombs', given by the students."[24]

Whether the members of the faculty committee, with the exception of Abeljanz, were aware of this situation is not clear. Should they nevertheless have had doubts about Werner's qualifications, these doubts vanished after they listened to his lecture and later heard the favorable comments from experts about Werner's article "Beitrag zur Konstitution anorganischer Verbindungen" (Figure 3), comprising 64 pages, which was published in the first issue of *Zeitschrift für Anorganische Chemie* in 1893.[25] Werner probably knew about the conditions of the laboratories, but was hopeful that after he had accepted the call the cantonal government would address the situation. In the next years, however, his hope was not fulfilled, and even after he was promoted to Ordinarius (full professor) in 1895 and turned down attractive calls to positions in Bern (1897), Vienna (1900), and Basel (1902), it took two more years for the Kantonsrat (the parliament of the canton of Zurich) to propose a new building for the Chemische Universitätsinstitut, which was approved in 1905 by the Zurich citizens in a vote "which was overwhelmingly favorable".[11] The laboratories of the new institute, built in the art nouveau style (Figure 4) and located practically opposite the main building of the University, were finished in 1909 and were among the best-equipped in the world at that time.



Beitrag zur Konstitution anorganischer Verbindungen.

Von

Alfred Werner.

Mit 17 Figuren im Text.

Unter Metallammoniaksalzen versteht man Verbindungen, welche aus Metallsalzen dadurch entstehen, daſs sich in ihr Molekül Ammoniakmoleküle einschieben, oder besser: Metallammoniaksalze sind Verbindungen, welche nach derselben Reaktion aus Ammoniak und Metallsalzen entstehen, nach der sich Chlorammonium aus Salzsäure (welche letztere ja das Haloidsalz des Wasserstoffes ist) und Ammoniak bildet.

Die Metallammoniaksalze nach ihrer Beständigkeit in verschiedene Verbindungsklassen einteilen zu wollen, von denen die beständigen atomistische Konstitutionsformeln, die unbeständigen sogenannte Molekülformeln erhalten würden, erscheint beim heutigen Stande der Wissenschaft als unzulässig; wir müssen nach einem anderen Einteilungsprinzip suchen. Ein solches ergiebt sich denn auch mit Leichtigkeit, wenn wir die empirische Zusammensetzung der Verbindungen und gewisse Eigenschaften der zu betrachtenden Körper als leitende Momente der Einteilung benutzen.

Als erste Klasse erhalten wir dann Verbindungen, welche auf ein Metallatom sechs Ammoniakmoleküle[1] enthalten oder sich von diesen ammoniakreichsten nach bestimmten, später zu besprechenden Regeln ableiten lassen.

Die zweite Klasse wird gebildet durch Verbindungen, welche auf ein Metallatom vier Ammoniakmoleküle enthalten, und solchen, die sich auch wieder von diesen Körpern in bestimmter Weise ableiten lassen.

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[1] Verbindungen, welche mehr als sechs Moleküle Ammoniak auf ein Metallatom enthalten, sind bis jetzt nur in äuſserst wenigen Fällen nachgewiesen, und bedürfen die betreffenden Körper noch näherer Untersuchung.

Figure 3. Front page of Werner's paper in *Zeitschrift für anorganische Chemie* (from Ref. [25]).

Figure 4. The Chemical Institute of the University of Zurich at Rämistrasse 74–76, which housed the Chemistry Department until it moved to the present Campus Irchel (photograph from Ref. [29]).

Although the title of the celebrated article sounded somewhat dull,[25] and—as Gerold Schwarzenbach assumed—the theoretical concept was probably understood "by only a very few people",[26] Werner's ideas led to a "paradigm shift".[27] When something like this happens, dramatic stories often emerge and this is true also here. Paul Pfeiffer, one of Werner's closest associates, who frequently discussed the stereochemistry of the ammine metal complexes with him,[28] reported that Werner said that the decisive idea hit him one night like "a flash", and that he immediately arose from his bed and wrote down the most important aspects of his idea in one stroke.[29] The vivacity of the wording in the article makes this story plausible and therefore we should assume this to be true.

This flash of genius was indeed not only the beginning of a unique scientific career but also sparked research activity far beyond the Swiss borders. Within a few years, undergraduates and doctoral students came to Zurich from all parts of Europe, soon after also from the U.S. and Japan, despite the unpleasant conditions in the Laboratorium A (Figure 5). Paul Karrer, who worked for his dissertation entitled "Über Valenzisomerie beim Kobalt" with Werner and got his PhD in 1911, recalled that "the great lecture hall [of the chemical institute], equipped for an audience of about 130, finally had to accomodate almost twice that number".[6] Until his retirement due to illness, Alfred Werner supervised 230 doctoral dissertations; 46 doctoral students (among them 1 woman) came from Switzerland and 179 (among them 21 women) from foreign countries. The nationality of the remaining 5 is unknown.[30] As Conrad Hans Eugster, Professor of Organic Chemistry at the University of Zurich from 1963 to 1988, aptly remarked many years later, the tremendous development of chemistry at Zurich University at the beginning of the 20th century was largely due "to the genius of Werner".[11]

Figure 5. Alfred Werner with some of his co-workers 1911. At the far left is Paul Karrer, Werner's successor in 1919 as Director of the Chemical Institute of the University of Zurich and winner of the Nobel Prize in Chemistry in 1937. At the far right is Dr. Chana Weizmann, a sister of Chaim Weizmann, the first President of the State of Israel (photograph from Ref. [27]).

However, one should not forget that despite the high regard which Werner received on his visits abroad and which finally culminated in the award of the Nobel Prize for Chemistry in 1913, in the first two decades of his scientific career several notable experts opposed, often violently, his ideas on the stereochemistry of the so-called "molecular compounds". Particularly, the majority of the coordination chemists at the time was not prepared to break with tradition. Right from the beginning, Werner's chief adversary was Sophus Mads Jørgensen, Professor of Chemistry at the Polytekniske Laereanstalt and the Universitet København from 1871 to 1908. Jørgensen dedicated his lifelong studies to the chemistry of ionic inorganic complexes, with an emphasis on the ammine complexes of cobalt, chromium, rhodium, and platinum, most of which he prepared for the first time.[31] Jørgensen's structural proposals for those complexes, which he investigated in more detail, were based on the concept developed by the Swedish chemist Christian W. Blomstrand in his influential book *Die Chemie der Jetztzeit* (The Chemistry of the Present), which from about 1870 on was widely accepted by coordination chemists and referred to as "Kettentheorie" (chain theory). Blomstrand's theoretical concept followed Kekulé's "Valenzlehre", suggesting that the valences of the atoms should have their smallest possible values. As a consequence, in the ammonia complexes, for example, $CrCl_3{\cdot}6NH_3$, and in the hydrates, for example, $CuSO_4{\cdot}4H_2O$, the respective NH_3 and H_2O groups should form chains similar to the CH_2 units in the aliphatic hydrocarbons. Since Kekulé had also postulated that in the diazo compounds the two halves of the molecule are connected by means of a direct nitrogen–nitrogen bond, Blomstrand also assumed that analogous N−N bonds exist in the oligomeric NH_3 chains of the ammonia complexes.

In spite of the resulting coordination number of five for nitrogen, Jørgensen was convinced of the correctness of Blomstrand's concept and dedicated all his efforts to its validation. Since it was known that in the hexaammine complex $CoCl_3$ $6NH_3$ three, in the pentaammine complex $CoCl_3{\cdot}5NH_3$ two, and in the tetraammine complex $CoCl_3{\cdot}4NH_3$ only one of the chlorine atoms could be precipitated with silver salts, Jørgensen concluded that those chlorine atoms are weakly linked to the NH_3 molecules and thus easily displaced (see Figure 6). In contrast, he considered the metal–chlorine bonds as inert, which would explain why these were not cleaved upon addition of silver salts. This proposal failed, however, in the case of the trisammine complex $CoCl_3$ $3NH_3$, which initially did not bother Jørgensen at all. In his first comprehensive critical reply to Werner's paper[25] he declared, that "a criticism of Werner's system was not the purpose of this work", which should only prove "that all the objections to his own theory of the ammonia metal compounds, which even such a skilful theoretician like Werner had put forward, are not correct."[32] Again it had

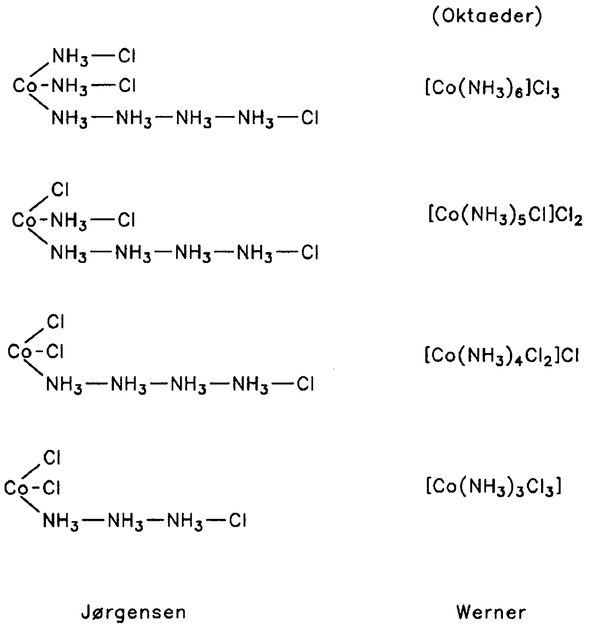


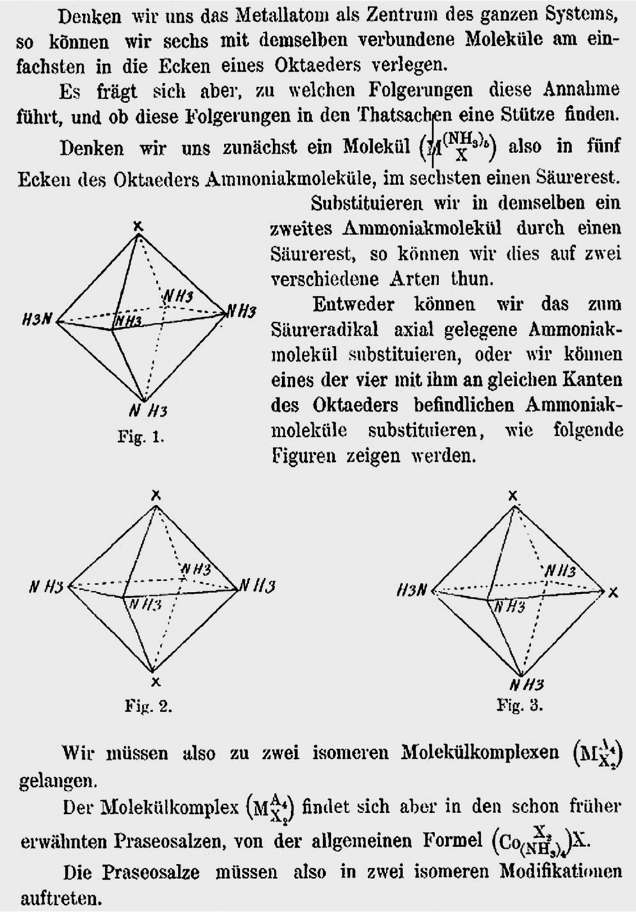
Figure 6. Comparison of the structures proposed by Jørgensen and later by Werner for the ammine cobalt(III) complexes studied by Jørgensen (from Ref. [27]).

been shown, “that intellectual speculations are not sufficient to construct a priori a theory for the ionic ammonia metal compounds. Only ‘unbiased experiments’ will be able to resolve the complicated identity of this extensive group of compounds.”.[32]

In mentioning “unbiased experiments”, Jørgensen addressed an apparent weakness of Werner’s paper, which was also recognized by several supporters of the new coordination theory. The reason was that Werner, in contrast to Jørgensen, could not justify his ideas about the structure of the ammine and aqua metal complexes with reference to experiments he had carried out himself.[33] In agreement with most of his contemporaries, Werner suggested that it would be appropriate to divide chemical compounds into two categories: compounds of first order and compounds of higher order—the so-called molecular compounds. In contrast to compounds of first order (comprising the halides, oxides, sulfides, nitrides, hydrides, etc.), Werner felt that the molecular compounds (including the ammine and aqua metal complexes) “had been somewhat neglected during the epochal phase of the organic chemistry, in which the structural theory was developed”.[34]

The basic assumption of Werner’s conceptual framework was that the central atoms in the compounds of first order are unsaturated with regard to the number of bonds, which means that they still have free “Affinitätsbeträge”, and thus are able to combine with other molecules. He called those forces “Nebenvalenzkräfte” (secondary valencies), which similar to the “Hauptvalenzkräfte” (primary valencies) of compounds of first order were effective from atom to atom. As each element has a highest “Hauptvalenzzahl” (oxidation number), it also has a highest “Nebenvalenzzahl”, which can be different from element to element. For the Nebenvalenzzahl he created the term “Koordinationszahl” (coordination number), which became one of the cornerstones of his theory.

The second, even more important cornerstone was his view on the spatial constitution, in other words, the stereochemistry of the molecular compounds, the topic that interested him most.[27] Since all the ammine cobalt(III) and chromium(III) complexes known at that time, which were mainly prepared by Jørgensen, had the coordination number six, Werner assumed that the octahedron is the most suitable polyhedron around the central metal atom. With this proposition, he could well explain the observed isomerism of sixfold coordinated complexes. In his monumental first paper, his ideas about the structure of compounds of the general composition $[M(NH_3)_4X_2]X$ are shown on page 298 (Figure 7).[25] Werner also drew attention to the fact that—not for the ammonia complexes $[Co(NH_3)_4X_2]X$,[35] but, based on Jørgensen’s work, for the ethylenediamino analogues $[Co(en)_2X_2]X$—two isomeric series exist (“praseo” and “violeo” salts, representing the *trans* and the *cis* isomers), which typically differ in their colors, green and violet, respectively.



Denken wir uns das Metallatom als Zentrum des ganzen Systems, so können wir sechs mit demselben verbundene Moleküle am einfachsten in die Ecken eines Oktaeders verlegen.

Es frägt sich aber, zu welchen Folgerungen diese Annahme führt, und ob diese Folgerungen in den Thatsachen eine Stütze finden.

Denken wir uns zunächst ein Molekül $\left(M^{(NH_3)_5}_{X}\right)$ also in fünf Ecken des Oktaeders Ammoniakmoleküle, im sechsten einen Säurerest.

Substituieren wir in demselben ein zweites Ammoniakmolekül durch einen Säurerest, so können wir dies auf zwei verschiedene Arten thun.

Entweder können wir das zum Säureradikal axial gelegene Ammoniakmolekül substituieren, oder wir können eines der vier mit ihm an gleichen Kanten des Oktaeders befindlichen Ammoniakmoleküle substituieren, wie folgende Figuren zeigen werden.

Fig. 1.

Fig. 2.

Fig. 3.

Wir müssen also zu zwei isomeren Molekülkomplexen $\left(M^{A_4}_{X_2}\right)$ gelangen.

Der Molekülkomplex $\left(M^{A_4}_{X_2}\right)$ findet sich aber in den schon früher erwähnten Praseosalzen, von der allgemeinen Formel $\left(Co^{X_2}_{(NH_3)_4}\right)X$.

Die Praseosalze müssen also in zwei isomeren Modifikationen auftreten.

Figure 7. Excerpt from Werner’s paper with the description of the *cis*/*trans* isomerism at the octahedron (from Ref. [25], p. 298).

Werner also offered a plausible explanation for the known isomerism of the platinum(II) complexes $[Pt(NH_3)_2Cl_2]$ and $[Pt(PEt_3)_2Cl_2]$, which also differ in color (yellow and white). In contrast to Jørgensen, who described the two isomers of the ammonia complex as $Pt(-NH_3-Cl)_2$ and $Pt(-NH_3-NH_3-Cl)Cl$, Werner assumed that the four ligands were directly bound to the metal and arranged in a square-planar fashion, and that the isomerism is due to the *cis* and *trans* position of the ammonia and chloro ligands. With the proposed square-planar coordination geometry, he could also explain why the reaction of the ammonia complexes with pyridine (py) yielded two isomers of the composition $[Pt(NH_3)_2(py)_2]Cl_2$ with *cis*- and *trans*-oriented NH_3 and pyridine ligands.[25] As was recently emphasized again,[36] this was the first time that for a compound of the type AB_2C_2 a square-planar arrangement of molecules or ions B and C around a central atom A was postulated, including all the possibilities which result for the formation of isomers.

It has already been mentioned, that despite Werner’s persuasive arguments the response to his ideas was quite mixed. The main reason was “the boldness of the new ideas and the ‘organic’ orientation of most of his colleagues at that time”.[37] Moreover, Jørgensen continued with his criticism and in a second, again monumental paper he not only published new experimental results,[38] but also expressed his doubt of the significance of conductivity measurements carried out by Miolati and Werner[39] with the ammine cobalt and platinum complexes. Werner responded immediately[40] and first refuted Jørgensen’s assertion that “his theory had received great applause from some people” but not “from those who had studied in more detail the chemistry of the ammonia metal salts".[38] Secondly, once more he pointed out the analogy in the different levels of conductivity measured for the isomeric series of octahedral cobalt(III) and platinum(IV) complexes. Somewhat later, he also reported his own synthetic experiments and compared his results with those of Jørgensen.[38] He emphasized the fact that similar to Jørgensen's $[Co(en)_2X_2]X$ compounds the ammonia complexes $[Co(NH_3)_4X_2]X$ also formed the expected two isomers, and that in both cases the *trans* isomer is more stable than the *cis* counterpart.[40,41]

Jørgensen did not yield but his opposition towards Werner's ideas became less vociferous.[42,43] Nevertheless, it is likely that until his death in 1914 he did not fully accept Werner's coordination theory,[44] which remains valid even today.[45] In his continuing studies, Werner focussed on putting his conceptual framework on a firm experimental basis. Two highlights of his further investigations were 1) the proof of his prediction, already made in 1899[46] and confirmed by his doctoral student Victor L. King in 1911, that cationic species *cis*-$[Co(en)_2X_2]^+$ or *cis*-$[Co(en)_2(NH_3)X]^{2+}$ form two enantiomers,[47] and 2) that this was also true for the tetranuclear complex $[Co\{(\mu\text{-}OH)_2Co(NH_3)_4\}_3]Br_6$ (Figure 8).[48,49] This result even convinced Werner's last sceptics, who had assumed that the existence of enantiomers of *cis*-$[Co(en)_2(NH_3)Cl]^{2+}$ was due to the carbon atoms of the ethylenediamino ligands.

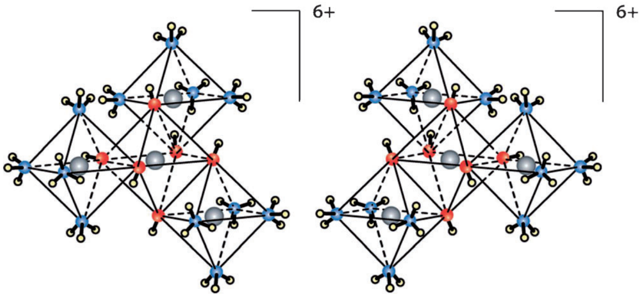


Figure 8. Structure of the enantiomeric cations of the carbon-free tetranuclear complex $[Co\{(\mu\text{-}OH)_2Co(NH_3)_4\}_3]Br_6$ (from Ref. [12]).

The decision of the Nobel Prize committee to award the Nobel Prize for Chemistry in 1913 to Alfred Werner met with worldwide approval. In the statement of the committee it was said that Alfred Werner received the prize "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".[50] In agreement with the ending of the last sentence, Werner also accentuated in his speech at the ceremony in Stockholm, that through his work further "opportunities for the investigation of new fields in inorganic chemistry, which are promising" would be opened up.[34] Moreover, he proposed (several years before Brønsted and Lowry) a new definition of acids and bases, which he derived from the reactivity of hydroxo and aqua metal complexes,[51] and he pointed out the analogies in the structure of these complexes with those of minerals such as the apatites or the Schweinfurter Green. Most remarkably, he also suggested subdividing the periodic system of the chemical elements into periods of different length and inserting two consecutive periods with 18 elements after two short periods with 8 elements.[34,52]

After he returned from Stockholm to Zurich, he was honored by institutions, colleagues, co-workers and, particularly, students in a manner that clearly and convincingly expressed their pride in the laureate.[11] In his honor, the Swiss Chemical Society organized a special meeting in Neuchâtel and founded the Werner Prize for young scientists, which is still awarded every year. The number of Werner's further awards is enormous and listed in Kauffman's monograph, which appeared on Werner's 100th birthday in 1966.[8] It is a real tragedy that already at the time he received the Nobel Prize, the laureate suffered from heavy headaches, lasting for days at a time, probably caused by "excessive working, high consumption of cigars, abuse of alcohol and stress of all sorts".[11] From summer 1915 on he applied several times to the cantonal authorities for reconvalescence leave, but he remained in poor health with the consequence, that on October 15, 1919 he resigned from his position. One month later, on November 15, 1919 he died in Zurich.

Although Alfred Werner was active in research for less than three decades, he created a seminal work, which is nearly without precedent in its breadth and depth. His pioneering studies on the constitution of inorganic compounds[25] not only revolutionized the basic concepts of coordination chemistry (e.g., had pushed all previous ideas about the structure and bonding of coordination compounds aside),[53] but also built a firm bridge to organic chemistry, in particular to the stereochemistry of molecular organic compounds.[36,37,54] Even Dmitri I. Mendeleev was "perfectly aware of this inherent connection",[26] and Gilbert N. Lewis, founder of the Lewis-acid/Lewis-base concept, wrote in his famous book *Valence and the Structure of Atoms and Molecules*, which appeared in 1923, "… in attempting to clarify the fundamental ideas of valence, there is no work to which I feel so much personal indebtedness as to this of Werner's".[55] The statement of John C. Bailar, a pioneer of modern coordination chemistry in the U.S., which he wrote in his article for the commemorative publication dedicated to Alfred Werner's 100th birthday, that "none of the postulates of the theory which he promulgated in 1893 have been found to be wrong" remains to be true to date.[56] And finally, the prophetic prediction made by Paul Pfeiffer in his obituary for Werner almost 100 years ago, that "Werner's ideas will have a decisive influence on the development of our science and will continue to fertilize it for a long time" has also been confirmed.[57]

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[1] L. Horner, *Helv. Chim. Acta* ***1967***, *50, Supplement 1,* 93–116.

[2] Evidence for this was the decision to do his PhD research under the supervision of Arthur Hantzsch and the titles of his first publications as well: a) "Über die räumliche Anordnung der Atome in stickstoffhaltigen Molekülen" (On the Spatial Orientation of Atoms in Nitrogen-Containing Molecules): A. Hantzsch, A. Werner, *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 11 – 30; b) "Bemerkungen über stereochemisch isomere Stickstoffverbindungen" (Comments on Stereochemically Isomeric Nitrogen Compounds): A. Hantzsch, A. Werner, *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 1243 – 1253; c) "Über ein zweites Benzoinoxim"(On a Second Benzoin Oxime): A. Werner, *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 2333 – 2236; d) "Über zwei stereochemisch isomere Derivate des Furfuraldoxims" (On Two Stereochemically Isomeric Derivatives of Furfural Oxime): A. Werner, *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 2336 – 2339.

[3] a) G. B. Kauffman indicated that 45 of Werner's 173 publications focused on topics in organic chemistry.[4] Even five decades after they had been published, his papers on the mechanism of the Walden inversion[3b,c] are still state of the art. b) A. Werner, *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 873 – 882; c) pages 68 – 72 in A. Werner, *Justus Liebigs Ann. Chem.* **1912**, *386*, 1 – 272.

[4] G. B. Kauffman, *J. Chem. Educ.* **1966**, *43*, 155 – 156.

[5] Over the years, I have been asked several times, particularly by non-German speeking colleagues, whether I am a relative of Alfred Werner, which I had to deny. Sometimes the reason for the assumption was the similarity of the names of our birth places, whereby it was not noticed that I was born in Mühlhausen but Alfred Werner in Mulhouse (German name from 1871 to 1918: Mülhausen). Franz Hein, my first mentor, encouraged me already in the late 1950s to make enquiries regarding a relationship which, however, remained unsuccessful.

[6] a) P. Karrer, *Helv. Chim. Acta* **1920**, *3*, 196 – 224; b) Facsimilae: P. Karrer, *Helv. Chim. Acta* ***1967**, 50, Supplement 1,* 7 – 23.

[7] Albert Einstein chose to study at the Eidgenössische Polytechnikum for the same reason.[26

[8] G. B. Kauffman, *Alfred Werner—Founder of Coordination Chemistry*, Springer, Berlin, **1966**.

[9] Arthur Hantzsch (1857–1935) and Alfred Werner were good friends. The friendship also remained firm after Hantzsch (Professor at the Polytechnikum in Zürich since 1885) accepted the call to the University of Würzburg to succeed Emil Fischer (1852–1919) in 1893, and after he moved 10 years later to the University of Leipzig to succeed Johannes Wislicenus (1835–1902). Hantzsch and Werner corresponded regularly and, when possible, met several times each year. G. B. Kauffman, who had the chance to read letters sent from Hantzsch to Werner,[8] concluded that "despite Hantzsch's more than five hundred publications, his greatest discovery was probably Alfred Werner".

[10] Hantzsch's esteem for Werner since the beginning of their collaboration is, for example, well manifested by Hantzsch's decision to add to their first joint paper[2a] the postscript: "The undersigned only fulfills his obligation to fairness by declaring that, in the case that the results described above have important consequences of some kind, the theoretical framework published by himself and Mr. A. Werner is in all its decisive parts the intellectual property of Mr. Werner. He alone formulated the fundamental ideas with its important conclusions already at a time, when it was mentioned in vague comments from others, that nitrogen possibly could give geometrical isomers similarly to carbon."

[11] "150 Jahre Chemie an der Universität Zürich": C. H. Eugster, *Chimia* **1983**, *37*, 194 – 237.

[12] K.-H. Ernst, F. R. W. P. Wild, O. Bracque, H. Berke, *Angew. Chem.* **2011**, *123*, 10970 – 10977; *Angew. Chem. Int. Ed.* **2011**, *50*, 10780 – 10787.

[13] a) G. B. Kauffman described Hantzsch as "slender, reserved, abstemius and controlled", whereas Werner "inclined toward corpulence, was hearty and robustly humorous in company, well-known for his enjoyment of alcohol and tobacco, and at times impulsive"; b) Ref. [8], p. 16.

[14] E. Berl, *J. Chem. Educ.* **1942**, *19*, 153 – 154.

[15] The *Schweizerische Schulrat* was paramount to the rector's office of the Eidgenössische Polytechnikum; and was in charge approving credits, confirming appointments, and awarding teaching qualifications. After the founding of the École Polytechnique Fédérale de Lausanne the *Schweizerische Schulrat* became in charge of both Federal Technical Universities.

[16] Ref. [8], p. 21.

[17] a) In German: "Die Affinität ist eine, vom Centrum des Atoms gleichmässig nach allen Teilen seiner Kugeloberfläche wirkende anziehende Kraft. Aus dieser Auffassung der Affinität folgt nothwendig, dass gesonderte Valenzeinheiten nicht bestehen. Die Valenz bedeutet eine von Valenzeinheiten unabhängiges, empirisch gefundenes Zahlenverhältniss, in welchem die Atome sich miteinander verbinden". And as subscript: "Dem Einwurf, dass durch die Annahme von Valenzeinheiten die Zahlenverhältnisse, in welchem die Atome sich miteinander verbinden erklärt werden, muss entgegengehalten werden, dass eine derartige Vorstellung keine Erklärung sondern nur eine Umschreibung dieser Erscheinung bedeutet. b) Werner's *Habilitationsschrift* is written in German *Kurrentschrift* and page 9 of it is reproduced in Kauffman's monograph (Ref. [8], p. 22).

[18] a) A. Werner, *Ber. Dtsch. Chem. Ges.* **1892**, *25*, 27 – 48; b) A. Werner, *Ber. Dtsch. Chem. Ges.* **1893**, *26*, 1561 – 1567.

[19] Ref. [8], p. 23.

[20] The Polytechnikum as well as later the ETH was organized not in faculties but in divisions. The *Laboratorium für Anorganische Chemie*, of which the most prominent chairman was Gerold Schwarzenbach (1904–1978) in the second half of the 20th century, today belongs to the Department of Chemistry and Applied Biosciences.

[21] Starting in 1902, after the faculty had intervened and the cantonal administration had issued a decree, the main inorganic lecture was given by Werner and not by Abeljanz.[11]

[22] Ref. [8], pp. 77–80.

[23] This happened quite soon thereafter: In 1895 Hans von Pechmann received the call to the chair of chemistry at the University of Tübingen.

[24] a) In German: ".. äusserst primitiv und unzugänglich, … die Doktoranden waren auf roh ausgebaute ehemalige Keller und Holzbehälter verwiesen, in denen auch um die Mittagsstunde künstliche Beleuchtung notwendig war … Der kalte, zementierte Kellerboden, die schlechte Heizung und die Unmöglichkeit einer richtigen Ventilation machten diese Räume in hohem Grade ungesund. Sie verdienten den Namen Katakomben, den die Studierenden ihnen beigelegt hatten, mit vollem Recht"; b) Ref. [6], pp. 10–11.

[25] A. Werner, *Z. anorg. Chem.* **1893**, *3*, 267 – 330.

[26] G. Schwarzenbach, *Helv. Chim. Acta* ***1967**, 50, Supplement 1,* 38 – 63.

[27] L. H. Gade, *Chem. Unserer Zeit* **2002**, *36*, 168 – 175.

[28] Paul Pfeiffer (1875–1951) did earned his PhD under the supervision of Alfred Werner in 1898. After he finished his dissertation entitled "Molekülverbindungen der Halogenide des 4-wertigen Zinns und der Zinnalkyle" (Molecular Compounds of the Halides of Tin(IV) and of Tin Alkyls), he worked for one semester with Wilhelm Ostwald at Leipzig and then with Arthur Hantzsch at Würzburg and returned to the University of Zurich for the Winter semester 1900/01. After he finished his Habilitation at Zurich one year later, he became Lecturer and was promoted to Associate Professor in Theoretical Chemistry in 1908. In rapid order, he became the Director of the Chemical

Institutes at Rostock in 1916, at Karlsruhe in 1919, and at Bonn in 1922, where he stayed until his retirement in 1947.

[29] P. Pfeiffer, *J. Chem. Educ.* **1928**, *5*, 1090 – 1098.

[30] Paul Karrer mentioned that the unusually high number of female doctoral students and PhD chemists at that time was due to the fact that since the winter semester 1868/69 female students could immatriculate at the University of Zurich.[6]

[31] G. B. Kauffman, *J. Chem. Educ.* **1959**, *36*, 521 – 527.

[32] a) In German: "daß geistreiche Spekulationen nicht genügen, eine Theorie der Metallammoniaksalze a priori zu konstruieren. Erst 'dem unerbittlichen Versuche' wird es allmählich gelingen, über die verwickelten Verhältnisse dieser ausgedehnten Gruppe von Verbindungen Klarheit zu verbreiten";[32b] b) S. M. Jörgensen, *Z. Anorg. Allg. Chem.* **1894**, *5*, 147 – 196.

[33] a) One of Werner's "northern colleagues" once told him that it is not so wrong to describe his intuitively formulated ideas as an "ingenious impudence"; b) Ref. [8], p. 30.

[34] Nobel Lecture held December 11, 1913 in Stockholm; see: A. Werner, *Helv. Chim. Acta* ***1967****, 50, Supplement 1,* 24 – 35.

[35] a) The French chemist E. Fremy, who studied extensively the chemistry of ammine metal complexes some decades prior to Jørgensen, characterized those ionic complexes according to their color as praseo, luteo, roseo, purpureo, violeo, and xantho salts; see: b) E. Fremy, *Ann. Chim. Phys.* **1852**, *35*, 257 – 311; E. Fremy, *J. Prakt. Chem.* **1852**, *57*, 81 – 106.

[36] L. H. Gade, *Z. Anorg. Allg. Chem.* **2012**, *638*, 247 – 248.

[37] P. Pfeiffer, *Angew. Chem.* **1920**, *33*, 37 – 39. This aspect was extensively discussed also by L. H. Gade.[27] The structure of the octahedral complexes drawn by Werner follow the ideas of van't Hoff and Le Bel about the stereochemistry of the tetracoordinated carbon atom.

[38] S. M. Jörgensen, *Z. Anorg. Allg. Chem.* **1894**, *7*, 289 – 330.

[39] a) A. Werner, A. Miolati, *Z. Phys. Chem.* **1893**, *12*, 35 – 55; b) A. Werner, A. Miolati, *Z. Phys. Chem.* **1894**, *14*, 506 – 521.

[40] A. Werner, *Z. Anorg. Allg. Chem.* **1895**, *8*, 153 – 188.

[41] A. Werner, *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 4817 – 4825.

[42] In a later publication (S. M. Jörgensen, *Z. Anorg. Allg. Chem.* **1899**, *19*, 109 – 157), Jørgensen denied any insulting intention of his statement.

[43] Werner was always careful to make sure that the objective differences with Jørgensen would not lead to personal disputes. Thus after receiving the Nobel Prize he attempted to visit Jørgensen in Copenhagen on his return from Stockholm to Zurich; however, this was not possible because Jørgensen was very ill.[6]

[44] a) F. A. Cotton, *J. Chem. Soc. Dalton Trans.* **2000**, 1961 – 1968; b) B. Spingler, M. Scavany-Grigorieff, A. Werner, H. Berke, S. J. Lippard, *Inorg. Chem.* **2001**, *40*, 1065 – 1066; c) E. Meggers, *Eur. J. Inorg. Chem.* **2011**, 2911 – 2926.

[45] Ref. [12], p. 10972.

[46] A. Werner, A. Vilmos, *Z. Anorg. Allg. Chem.* **1899**, *21*, 145 – 158.

[47] King separated the enantiomers of $[Co(en)_2(NH_3)Cl]^{2+}$ via the diastereomeric (+)-bromocamphersulfonates. The separation was achieved without problems and the racemization, which Werner initially was afraid of, did not occur: A. Werner, V. L. King, *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 1887 – 1898.

[48] A. Werner, *Ber. Dtsch. Chem. Ges.* **1914**, *47*, 3087 – 3094.

[49] The special irony of this result is that the racemate of the tetranuclear complex was first prepared by Jørgensen: S. M. Jørgensen, *Z. Anorg. Allg. Chem.* **1898**, *16*, 184 – 197.

[50] See: http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1913/.

[51] Werner wrote in German: "… gelangen wir zu einer neuen Definition für die Basen, dahingehend, dass die Basen Verbindungen sind, welche die Fähigkeit besitzen, die Wasserstoffionen des Wassers zu ketten und dadurch das Gleichgewicht zwischen dem Wasser und seinen Ionen durch Aufnahme von Wasserstoffionen zu stören, was eine Vergrösserung der Hydroxylionenkonzentration zur Folge hat." See Ref. [34], p. 29.

[52] a) A. Werner, *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 914 – 921; b) A. Werner, *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 2022 – 2027.

[53] See also: G. B. Kauffman, *Bull. Hist. Chem.* **1997**, *20*, 50.

[54] U. Wannagat, *Chem. Unserer Zeit* **1967**, *1*, 24 – 27.

[55] G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, The Chemical Catalog Company, New York, **1923**.

[56] J. C. Bailar, *Helv. Chim. Acta* ***1967****, 50, Supplement 1,* 82 – 92.

[57] In German: "..that Wernersche Ideen noch auf lange Zeit hinaus einen starken Einfluß auf die Entwicklung unserer Wissenschaft ausüben und diese mächtig fördern werden."[37a]