

Alfred Werner

THE STRUCTURE OF PLATINUM COMPLEXES

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In 1828 G. Magnus obtained a salt with the empirical formula $\text{PtCl}_2 \cdot 2\text{NH}_3$ by the action of ammonia on platinum chloride. This was one of the first "metal-ammonia compounds" to be isolated, and it was followed during the next few decades by many similar compounds of bivalent and quadrivalent platinum and of chromium, cobalt and other metals. They were generally described loosely as "double compounds" or "molecular compounds" and since in the absence of any theory of their constitution they could not be assigned sys-

tematic names, they were often named after their discoverers.

By the late 1860s Kekulé and others had shown that organic molecules were built up of chains and rings of quadrivalent carbon atoms, and in 1869 the Swedish chemist C. W. Blomstrand (1826–1897) suggested that metal-ammonia compounds contained chains of quinquivalent nitrogen atoms, with the $-\text{NH}_3-$ group playing a part similar to that of the $-\text{CH}_2-$ group in organic compounds (1). Thus (2) the compound with the

Alfred Werner 1866–1919

Methods of separating and refining the platinum metals are largely based on the chemistry of their complex compounds. Werner's well known co-ordination theory, published in 1893, satisfactorily explained the structure of these compounds and enabled new compounds with predictable properties to be synthesised. Born a hundred years ago, Werner became Professor of Chemistry at Zürich at the age of only 26 and despite many invitations to accept chairs in other universities remained there all his working life. Many of his students worked on complex compounds and were largely responsible for the rapid advances in the chemistry of all the platinum metals in the early years of the century



The title page of Werner's classic paper, running to sixty-four pages, in which he put forward his co-ordination theory of complex compounds in 1893 in *Zeitschrift für anorganische Chemie*

Beitrag zur Konstitution anorganischer Verbindungen

Von
ALFRED WERNER
Mit 17 Figuren im Text

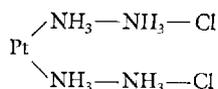
Unter Metallammoniaksalzen versteht man Verbindungen, welche aus Metallsalzen dadurch entstehen, daß sich in ihr Molekül Ammoniakmoleküle einschieben, oder besser: Metallammoniaksalze sind Verbindungen, welche nach derselben Reaktion aus Ammoniak und Metallsalzen entstehen, nach der sich Chlorammonium 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 ergibt 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.

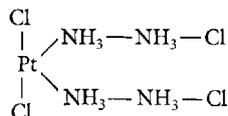
Als erste Klasse erhalten wir dann Verbindungen, welche auf ein Metallatom sechs Ammoniakmoleküle enthalten oder sich von diesen ammoniakreichsten nach bestimmten, später zu besprechenden Regeln ableiten lassen.

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.

formula $\text{PtCl}_2 \cdot 4\text{NH}_3$, which J. Reiset prepared by the further action of ammonia on Magnus's salt, was given the formula



and the related compound of quadrivalent platinum, $\text{PtCl}_4 \cdot 4\text{NH}_3$, was considered to be



In some such compounds the chlorine was only partly precipitated by silver nitrate, and the other halogens and radicals of oxyacids behaved similarly. This was explained by assuming that an atom or radical was reactive only at the end of a nitrogen chain, but not when attached directly to the metal. The theory of nitrogen chains was adopted and extended by the Danish chemist S. M. Jørgensen (1837-1914), who discovered a large number of new molecular compounds containing

ammonia and other bases. However, some of them were assigned structures only with great difficulty, and by the early 1890s the time was ripe for a new theory. It was provided by the chemist whose centenary is being celebrated this year.

Alfred Werner was born on December 12th, 1866, in Mulhouse, an industrial town in Alsace, which was French territory until 1871 when it was acquired by Germany and its inhabitants became German citizens (3). His father was a factory inspector who also cultivated a small farm, and he performed his first chemical experiments in a laboratory fitted up in a barn. During his military service in 1885-86 Werner attended lectures at the Karlsruhe Technische Hochschule and he determined to be a chemist. In 1886 he entered the Swiss Federal Polytechnic Institute in Zürich, and in a doctoral thesis prepared under the supervision of Otto Hantzsch he examined the stereochemistry of organic nitrogen compounds and proposed the theory of the tetrahedral nitrogen atom

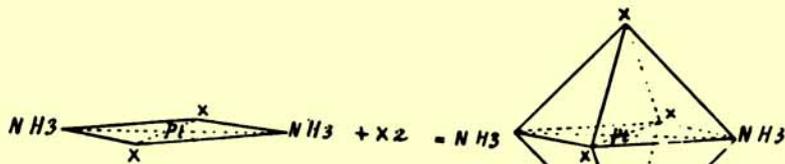


Fig. 14
Platosamminalze

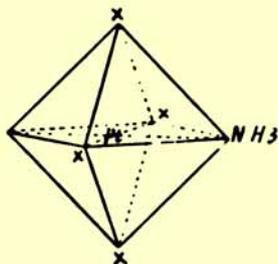


Fig. 15
Platiniamminalze

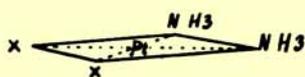


Fig. 16
Platosemidiamminalze

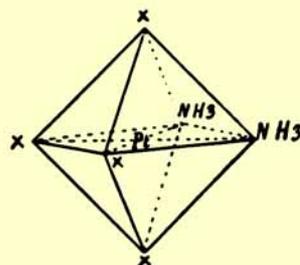


Fig. 17
Platinisemidiamminalze

*The first diagrams illustrating the stereochemistry of platinum
(From the 1893 paper in Zeitschrift für anorganische Chemie)*

that was amply confirmed by Hantzsch's subsequent researches (4).

After a few months studying thermochemistry with Berthelot in Paris, Werner returned to Zürich. In 1892 he began to teach at the Polytechnic, but a year later he was appointed professor of chemistry at the University of Zürich, and he remained there for the rest of his life. He adopted Swiss nationality in 1895, and he was the first president of the Swiss Chemical Society when it was founded in 1901.

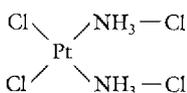
Werner began to be interested in the general problem of molecular structure while working under Hantzsch. In 1891 he published an interesting theory that valency did not always act in fixed directions but was to be considered as a force distributed over the surface of the atom, and he hoped to explain some organic structures and molecular rearrangements (5). However, he abandoned this work and turned his attention to the

metal-ammonia compounds, where he soon found defects in the chain theory, and in 1893 he proposed his well-known co-ordination theory in a paper modestly entitled "Contribution to the Constitution of Inorganic Compounds" (6).

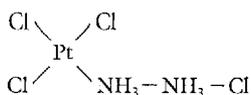
He found that in many compounds all the ammonia could be replaced one molecule at a time by univalent acid radicals which did not give their normal reactions and were therefore directly attached to the metal; this suggested that the ammonia molecules were themselves directly attached to the metal, and were not arranged in a chain. Arrhenius's theory of electrolytic dissociation, published in 1887, enabled Werner to give a satisfactory explanation of the fact that some acid radicals could not be readily detected: only radicals not attached to the metal were present in the solution as ions, and the others formed part of a complex which did not give the reactions of its components. He showed further that

the total number of ammonia molecules and univalent acid radicals in the complex was constant, generally four or six depending on the nature and valency of the metal, and he called this the co-ordination number.

Werner also considered the arrangement in space of the components of the complex, and he was able to account for several cases of isomerism that could not be satisfactorily explained by the chain theory. Magnus's salt, of empirical formula $\text{PtCl}_2 \cdot 2\text{NH}_3$, was shown to be $[\text{Pt}(\text{NH}_3)_4]\text{PtCl}_4$, and was quite distinct from two other compounds of the formula $\text{PtCl}_2 \cdot 2\text{NH}_3$. Both of these reacted with further chlorine to form isomers of $\text{PtCl}_4 \cdot 2\text{NH}_3$, which, according to the chain theory, were



and

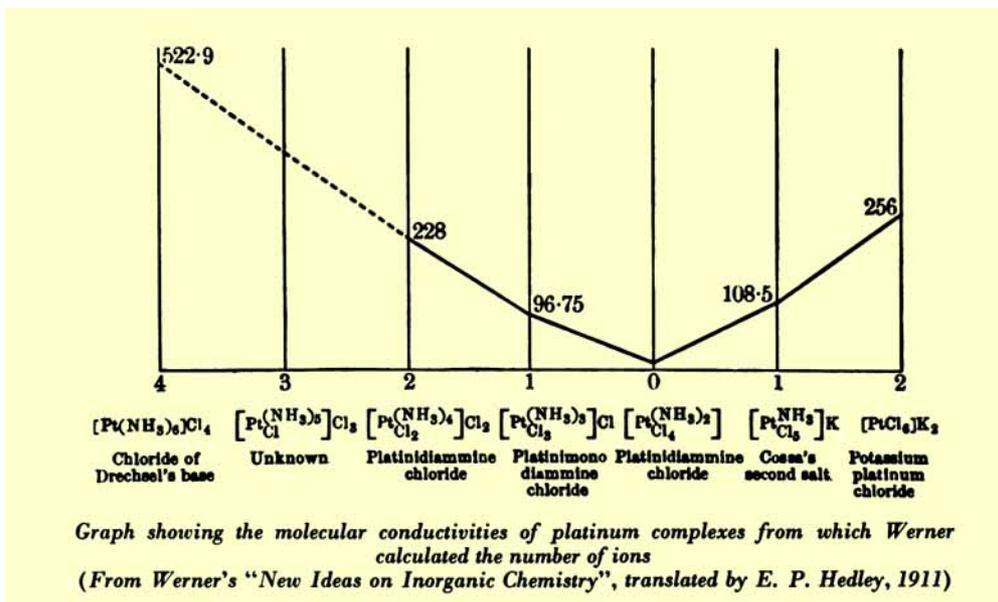


However, Werner showed that none of the chlorine in these compounds was ionic, and

all the chlorine atoms were therefore directly attached to the platinum. In the platinous compounds the co-ordination number was considered to be four, with a planar structure, and in the platonic compounds the co-ordination number was six and the structure octahedral. The relation between the isomers could thus be very elegantly represented as in the illustration opposite (7).

The entire co-ordination theory, with numerous examples, was presented by Werner in this important paper when he was still only twenty-six years old, and in the same year, 1893, he supported it with the first of a series of papers written in collaboration with his friend A. Miolati (8). They measured the molecular conductivities of many complex compounds and, applying Arrhenius's theory, they found that the number of ions always agreed with that required by the co-ordination theory. Their results for a series of platinum complexes were later republished in graphic form as shown below (9).

The new theory soon gained adherents, but it was not until 1907 that Jørgensen finally accepted it, when Werner prepared some cobalt compounds that were a necessary consequence of the co-ordination theory but not



of the chain theory. In 1911 Werner first obtained optical isomers of complexes that could be asymmetric only with an octahedral configuration, and this convinced most of his remaining critics, but it was not until 1935 that the planar configuration of platinum complexes was conclusively proved by the resolution of compounds that would be asymmetric if square, but not if they were tetrahedral (10).

Werner refused invitations to chairs in several other universities, and he built up a great research school at Zürich, where more than 200 doctorates were obtained under his immediate supervision. His students generally worked on complex compounds, and they were largely responsible for the rapid advance in the chemistry of all the platinum metals in the early years of the twentieth century. His great capacity for work enabled Werner to give several courses of lectures as well as supervise as many as twenty-five research students at one time. They also had to work hard, and he expected to find something new every time he visited them—twice a day! But outside the laboratory he had a friendly disposition, and he took a personal interest in the subsequent careers of his students, who came from many countries (11).

In his address on receiving the Nobel

Prize in 1913 Werner outlined the history of his theory, and gave ample credit to his former rival, Jørgensen, whose discoveries had formed the experimental basis of the theory in its early days (12). Experimental verification continued after 1913, and within a decade the co-ordination theory formed an essential part of the electronic theory of valency, but Werner did not live to see this come about.

In 1915 he began to show symptoms of arteriosclerosis, and he died on November 15th, 1919, at the age of 52.

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Supported Platinum Metal Catalysts

A REVIEW OF RUSSIAN RESEARCHES

While a great volume of literature is nowadays flowing from workers in the field of catalysis throughout Europe and the United States, a significant amount of work is also being published on this subject in the Soviet Union. The difficulty of keeping abreast with developments is great enough in the more generally understood languages, but is even more onerous with Russian papers. The recent enterprise in publishing full translations of Russian journals has, however, helped materially, a good example being an exhaustive review on supported platinum metal catalysts. This quite massive paper, by E. I. Gil'debrand, first published as

"Katalizatory na Nositoryakh" (*Trudy Inst. Khim. Nauk, Akad. Nauk Kaz. S.S.R.*, 1965, **13**, 67–117), and now available in English (*Internat. Chem. Engng.*, 1966, **6**, (3), 449–480), surveys over two hundred and forty published papers, the great majority of them of Russian origin.

Many aspects of the whole field of catalyst theory and practice are covered, starting with methods of preparation and the role of the support in determining catalytic properties, and going on to deal with methods of investigating the structure of supported catalysts and with both theoretical views and experimental data on their activity.