



Alfred Werner, initiator of modern inorganic stereo chemistry- A tribute in the occasion of 100th year of receiving the Nobel Prize by the great chemist

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Publication History

Received: 10 March 2013

Accepted: 12 April 2013

Published: 1 May 2013

Citation

Abhisek Saha. Alfred Werner, initiator of modern inorganic stereo chemistry- A tribute in the occasion of 100th year of receiving the Nobel Prize by the great chemist. *Discovery*, 2013, 4(11), 29-31

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ABSTRACT

Alfred Werner was born on December 12, 1866, at Mülhausen in Alsace. In 1913, he received the Nobel Prize for Chemistry. Werner's name will always be coupled with the theory of coordination which he established and also with his work on the spatial orientations of atoms in the inorganic molecule, the work he did, when he was only 24. Today coordination theory can be seen in accomplishment all over molecular compounds, organometallics, biomolecules, inorganic solids, minerals, catalysts and so on. He is sometimes called "the inorganic Kekule".

Keywords: Alfred Werner, Werner Coordination Theory, Jørgensen "chain theory".

1. INTRODUCTION

1.1. A brief sketch on Alfred Werner

Where is the similarity in between Rabindranath Tagore and Alfred Werner? This question can be asked in a quiz competition. Apparently it appears to us that there is no similarity in between a great poet and great chemist. But 1913 was an unforgettable year for each and every Indian; Rabindranath Tagore became the first Indian to be given the Nobel Prize for creating "insightful, speaking new and elegant poetry". And Alfred Werner became the first Swiss chemist to win it for throwing new insight on the association of atoms in inorganic molecules (Chakravorty et al.1999).

Alfred Werner, son of factory foreman JA. Werner and his wife Jeanne, née Tesche, was born on December 12, 1866, at Mülhausen in Alsace, where he went to school .he attended the École Libre des Frères (1872–78), followed by the École Professionnelle, a technical school where he studied chemistry (1878–85). He spent one year (1885–86) of compulsory military service in the German army at Karlsruhe. In 1886 he enrolled in the Eidgenössisches Polytechnikum (now the Eidgenössische Technische Hochschule [ETH], or Swiss Federal Institute of Technology) in Zürich, from which he received a technical chemical degree (1889).Werner received a doctorate formally from the University of Zürich in 1890.During his studies there he was influenced by professor A.Hantzsch. In 1889

he was selected assistant in professor Lunge's laboratory at the Zurich Technical High School and he then began to assist with Professor Hantzsch in research. In 1890 he took his degree in the University of Zurich with a thesis on the spatial arrangements of the atoms in molecules containing nitrogen (Kauffman et al.1966). Until 1891 he did more work on this subject area and visited Paris, where he worked under the supervision of Professor Berthelot at the Collège de France. In 1892 he returned to Zurich as a lecturer in the Technical High School, and in 1893 in 1895, at the age of twenty-nine he became the professor of Chemistry in the university, giving the lectures on organic chemistry until, in 1902, he took over the lectures on inorganic chemistry as well (Werner et al.1966). In 1894, Werner married Emma Giesker of Zurich, a member of a German family. They had one son, Alfred, and one daughter, Charlotte.

Werner was a friendly man, whose recreations were billiards, chess and the Swiss card game. He spent his holidays among the mountains and travelled much to attend scientific meetings outside Switzerland. As a lecturer he was a convincing speaker with a contribution for clear explanations of tricky problems. Valuable for others were his books *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (New ideas in inorganic chemistry) and *Lehrbuch der Stereochemie* (Textbook of stereochemistry), both published in 1904 (Cohen et al.1967).

Werner was corresponding member of the Royal Society of Sciences (Königliche Gesellschaft der Wissenschaften) at Göttingen and of the Physico-Medical Society (Physikalisch-medizinische Sozietät) of Erlangen. He was awarded an honorary doctorate by the University of Geneva, and was an Honorary Member of the Society of Physics and Natural History in the same town, of the Physical Association of Frankfurt/Main, of the German Bunsengesellschaft, of the Société Vaudoise des Sciences Naturelles at Lausanne, and of the Chemical Society of London. He was also a permanent member of the Imperial Society of Friends of Natural History, Anthropology and Ethnography of Moscow. France conferred upon him the Leblanc Medal of its Societe Chimique and the distinction of Officier de l'Instruction Publique. In 1913, the year in which he received the Nobel Prize for Chemistry, he was previously suffering from arteriosclerosis and by 1915 this had compelled him to give up his general lectures on chemistry and in 1919 he had to give up his Professorship. On November 15, 1919, he died at the early age of 53.

2. EARLY RESEARCH WORK BY ALFRED WERNER

Werner's first publication, a foundation stone of stereochemistry, based on his doctoral dissertation and written with his research supervisor, Arthur Hantzsch applied Joseph-Achille Le Bel and Jacobus Henricus Van't Hoff's perception of the tetrahedral carbon atom (1874) to the nitrogen atom. It explained several cases of *cis-trans* isomerism among trivalent nitrogen compounds such as the oximes, led to the breakthrough of new isomers, and placed the stereochemistry of nitrogen on a reliable theoretical establishment. In 1892 Werner became an unsalaried lecturer at the Polytechnikum upon acceptance of his original research paper required in order to teach at a university. In this work, which elicited little notice because it was published (1891) in a local journal, he proposed replacing August Kekule's firmly directed valence bonds in organic compounds with a more stretchy approach of viewing affinity as a variously separable force acting equally in all directions from the atom's centre.

August Kekulé, the ultimate of structural organic chemistry, had shown that carbon usually forms four bonds. Then in 1874 two young men, van't Hoff and Le Bel, proposed that these bonds are tetrahedrally inclined in space. And organic chemistry was experiencing great victory in the latter half of the 19th century. It is in this background that Werner started his research work. An honest urge towards the genuineness drove him. The act of spatial orientation of bonds (stereochemistry) as a special feature of carbon alone did not echo rational to him. Werner was inventing a new model in chemical science.

Werner's name will always be coupled with the theory of coordination which he established and also with his work on the spatial orientations of atoms in the inorganic molecule, the work he did, when he was only 24, for his doctorate thesis in 1892. In this work he gave the idea that, in the many compounds of nitrogen, the three valence bonds of the nitrogen atom are directed towards the three corners of a tetrahedron, the fourth corner of this being occupied by the nitrogen atom. In 1891 he had published a paper on the theory of affinity and valence, in which he substituted for Kekulé's idea of constant valence, the idea that affinity actually is an attractive force exerted from the centre of the atom which acts uniformly towards the entire parts of the Surface of the atom (Kauffman et al. 1997). In 1893 he declared, in a paper on mineral compounds, his theory of variable valence, in which inorganic molecular compounds contain single atoms which act as central nuclei around which are, arranged a definite number of other atoms, radicals or other molecules in a simple, spatial, geometric pattern. The figure which expresses the number of atoms thus grouped round a central nucleus was called by Werner the coordination number, the most important of these coordination numbers being 3, 4, 6 and 8, the number 6 occurring more frequently. A lot of molecular compounds correspond to the number 6 type, and in the greater part of these there is a central atom with coordinated atoms at the corners of an octahedron (Werner et al. 1911). For the next 20 years Werner and his collaborators extensively prepared new series of molecular compounds and studied their configurations. Finally, his work in the discovery of optically-active isomers of the complexes studied, the existence of which had been forecast by his hypothesis. More than 40 series of optically-active complexes with octahedral symmetry were separated in optically-active forms, with the result that the spatial configuration of the complexes to the coordination number 6 was established as firmly as that of the tetrahedral carbon atom of Van't Hoff and Le Bel. Werner also worked on complexes with other coordination numbers, in particular 4, for which the form can be tetrahedral or a plane square. As Paul Pfeiffer, in his account of Werner's work published in *Great Chemists* (1961, Edited by Eduard Farber, Interscience, New York) remarks the coordination theory of Werner extended all through the entire range of systematic inorganic chemistry and into organic chemistry also. For his work on it Werner was awarded the Nobel Prize for Chemistry for 1913 (Constable et al.2013).

At the time of its commencement, Werner's theory was mostly without experimental verification and the data that he cited in support of his ideas had been obtained by his primary scientific adversary, the Danish chemist Sophus Mads Jørgensen. Jørgensen adhered to the rival Blomstrand-Jørgensen "chain theory," which was ultimately outdated by Werner's theory, the foundation for modern coordination chemistry (Werner et al. 1966). Werner discarded Kekule's artificial distinction between "valence compounds," amenable to classical valence theory, and "molecular compounds," those not explainable by this theory. Werner proposed a revolutionary approach in which the constitution and configuration of metal-ammines (now called "Werner complexes"), double salts, and metal salt hydrates were logical consequences of a new concept, the coordination number. He divided metal-ammines into two classes—those with coordination number six, for which he postulated an octahedral configuration, and those with coordination number four, for which he proposed a square planar or tetrahedral configuration. He also postulated two types of valence—primary valence, which bonded the anion to the metal atom, and secondary valence, which bonded the ammonia to the metal atom. Werner demonstrated the validity of his views by citing numerous reactions, transformations, and cases of isomerism (Kauffman et al. 1966).

3. MAJOR THEORETICAL WORK BY THE WERNER

A historically important molecular compound, also called coordination compound or complex, is yellow colored $\text{CoCl}_3 \cdot 6\text{NH}_3$. Werner formulated it as the salt $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, where the six NH_3 molecules are coordinated to the central cobalt ion forming the complex cation $[\text{Co}(\text{NH}_3)_6]^{3+}$; its ionic charge being balanced by 3Cl^- . Here the coordination number is 6 and the geometry is octahedral. Coordination in terms of isomerism and other properties. All the chemistry was falling into a melodious pattern and finally in 1911, an asymmetric inorganic complex was resolved into optical isomers (so far a domination of carbon compounds) signifying the ultimate achievement of his belief (Cohen et al.1967).



Figure 1
Alfred Werner (1866-1919),
(<http://www.scientific-web.com>)

4. CONCLUSION

4.1. Importance of Werner Coordination theory

Today coordination theory can be seen in accomplishment all over molecular compounds, organometallics, biomolecules, inorganic solids, minerals, catalysts and so on. This is so because polyhedral arrangement of valence is deep-seated in the electronic structure of atoms as was shown by Linus Pauling and others years later. His ideas are applicable to almost the entire field of inorganic, organic, analytical, and physical chemistry, as well as biochemistry, geochemistry, and mineralogy (James et al. 1993).

SUMMARY

Alfred Werner was one of the first to show that stereochemistry is not limited to organic chemistry but is a general phenomenon. His coordination theory has had an effect on inorganic chemistry comparable to that exerted on organic chemistry by the ideas of Kekule, Archibald Scott Couper, Le Bel, and van 't Hoff. He is sometimes called "the inorganic Kekule". Later major universities of Europe became eager to take on him, but in vain. Dmitri Ivanovich Mendeleev who invented the foundation of elemental order, the periodic table (1869), once said that a true mover of inorganic chemistry has to be "a thinking creative artist". Alfred Werner remains the most notable example.

DISCLOSURE STATEMENT

There is no financial support for this review work from the funding agency.

ACKNOWLEDGMENT

Much thanks to Mrs. M. Saha for her constructive criticism, and assistance towards the successful completion of this review work

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