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'Counting ions' in Alfred Werner's coordination chemistry using electrical conductivity measurements

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ABSTRACT

From 1888 till 1892 Alfred Werner, the founder of coordination chemistry, developed together with his friend Arturo Miolati electrical conductivity of ionic complexes as an auxilliary analytical tool for structural elucidations of complexes. The used electrical conductivity device was based on a design of Wilhelm Ostwald consisting of a generator for alternating current (induction apparatus with Wagner hammer), a measuring cell with platinated electrodes and a rheostatic part including a buzzer for balancing resistivity conditions. Electrical conductivities were examined in the ion-isomeric series of $Pt(II)(NH_3)_nCl_2$ (n = 0 – 4), $Pt(IV)(NH_3)_nCl_4$ (n = 0 – 6) and $Co(III)(NH_3)_nCl_3$ (n = 0 – 6) complexes producing approximately V-shaped curves in dependence of the stoichiometry factor n. Replacing in the coordination spheres neutral Lewis base type ligands by 'anionic residues' generated charged complexes, which by conductivity measurements laid grounds for Alfred Werner's coordination theory [primary (from 'anionic residues') and secondary valencies (from Lewis bases)] and the Nobel Prize in 1913. From 1893 on seven PhD theses were prepared in Alfred Werner's group, which dealt with conductivity measurements establishing identification processes of complexes by 'ion counting'. In 1902 Alfred Werner ceased to apply electrical conductivity in his group switching to meanwhile more timely coordination chemistry fields.

KEYWORDS: Alfred Werner, Arturo Miolati, coordination compounds, Werner complexes, conductivity measurement, electrolytic dissociation, ion isomerism

Resumen ('Contando iones' en la química de coordinación de Alfred Werner con el uso de mediciones de conductividad)

Desde 1888 hasta 1892 Alfred Werner, el fundador de la química de coordinación, desarrrolló junto con su amigo Arturo Miolati la medición de conductividad eléctrica de iones complejos como una herramienta analítica auxiliar para la elucidación de la estructura de complejos. El aparato utilizado para la conductividad eléctrica estaba basado en un diseño de Wilhelm Ostwald, que consistía de un generador de corriente alterna (aparato de inducción con martillo de Wagner), una celda de medición con electrodos platinados y un componente reostático que incluía un timbre para balancear las condiciones de resistividad. Las conductividades eléctricas fueron examinadas en una serie de iones isoméricos complejos de $Pt(II)(NH_3)nCl_2$ (n = 0 – 4), $Pt(IV)(NH_3)nCl_4$ (n = 0 – 6) y de $Co(III)(NH_3)nCl_3$ (n = 0 – 6), que produjeron curvas en forma de V con dependencia en el factor estequiométrico, n. Al reemplazar en la esfera de coordinación ligantes neutros tipo base de Lewis por 'residuos aniónicos' se generaron complejos cargados, que por mediciones de la conductividad condujeron a Alfred Werner a la teoría de la coordinación [valencia primaria (proveniente de los 'residuos aniónicos') y secundaria (de las bases de Lewis)]. A partir de 1893, siete tesis doctorales fueron elaboradas por miembros del grupo de Werner en las que con mediciones de la conductividad establecieron el proceso de identificacion de complejos por 'conteo de iones'. A partir de 1902, Alfred Werner cerró la aplicación de la conductividad eléctrica en su grupo cambiando a otros temas más avanzados de la química de coordinación.

Palabras clave: Alfred Werner, Arturo Miolati, compuestos de coordinacion, comlejos de Werner, mediciones de conductividad, disociación electrolítica, isomerismo iónico

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Introduction

Short survey of Alfred Werner's life and personality

Alfred Werner is regarded as the founder of coordination chemistry. He took a whole field of chemistry from a dark and mystical perception to the level of a bright and rational being. To achieve this he was left only a short period of time by living an intense life, which was mainly dedicated to chemistry (Kauffman, 1979; 1994). Alfred Werner was a full heart scientist. All his endeavors were strongly curiosity-driven, which made him a steady searcher for novelties in science. The main sources of his chemical creativity were deductions by intuition and conceptual thinking, which made his research very effective. Connected to that many contemporaries reported that Alfred Werner was a man of great imagination and inspiration.

The main stages of his life are listed in the following compilation, which will be referred to in the later context of this article:

Alfred Werner's life

1866	Born in Mulhouse
1887	Enrollment as a student of chemistry at ETH Zürich
1889	Diploma of Chemistry from ETH Zurich
1890	Ph.D. with Prof. Hantzsch at ETH Zürich
1889	Alfred Werner meets A. Miolati
1892	Habilitation ETH Zürich, unsalaried Privatdozent
1893	Associate Professor, University of Zürich
1893	Formulation of Coordination Theory
1895	Full Professor, University of Zürich
1895	Marriage and Swiss Nationality
1905	First edition of Alfred Werner's book *Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie*
1909	New chemistry building in Zurich
1913	Nobel Prize
1915	Descent to Illness
1919	Death

Alfred Werner was a chemist always trying to look over the fence to other science fields. At his times physics was just at the turn to develop into a quantitative discipline, which attracted him very much. It was maybe his not so consciously expressed desire, but steadily pursued way in chemistry to take chemistry, particularly coordination chemistry, away from the world of qualitative and at the time often even ill-defined and mystical perceptions to a more quantitative and better defined science. The marriage of chemistry with physics is physical chemistry, which took place at around the beginning of Alfred Werner's scientific career in the 1880s along with the quantification trends in physis. Looking over the fence to physics meant for Alfred Werner to treat chemistry more quantitatively through physical measurements, but also to conceive it more conceptually and fundamentally.

A good, but not fully accomplished example for this latter notion are the developments of his coordination theory, which expresses indeed the trend to make the earlier Bloomstrand-Jorgensen coordination theory (Kauffman, 2003; Berke, 2009) more adjusted to the physical reality by transposing coordination chemistry from the two-dimensional space ('flat molecules') into the three-dimensional space inventing thus the stereochemistry of coordination compounds.

In this context and with the given conviction in mind Alfred Werner got aware of the fact that his new stereochemical views of coordination compounds needed also a new binding theory for complexes, which indeed he had then eventually created. He tried to reach a more quantitative view of inorganic and coordination chemistry (Werner, 1905), but in its essence Alfred Werner's binding theory could finally achieve that, even though it was not totally built on solid physical grounds. His coordination theory could serve as a heuristic representative method to extensively match reality with conclusions by analogy, but could not serve for more. An atomistic physical picture of the chemical bond did not exist at Alfred Werner's time, nor was it existent in fragments, which 'forced' Alfred Werner to strive for substitution of this deficiency from the physics side. Even though Alfred Werner's conceptual thinking was much ahead of his time and his 'coordination theory' created at the turn of the year 1892 (published in 1893) had finally attained consistency by itself, it could not cope with the factual physical level of say the times of the 1920^{th} when quantum physics had triggered the developments of a new picture of molecules. Alfred Werner's coordination theory did not reach the level of quantification and sophistication that it had needed in order to become comprehensive. This was for instance criticized at his time by his PhD student A. Pfeiffer, who became later on his colleague (Werner, 1923). Principally there was nothing wrong with his theory, but as said already the level of sophistication was not high enough to survive for good. Alfred Werner's theory served for about 20 years as a well-received inductive formula used as a valuable platform for the creation of ideas and explanations.

Another so to speak 'true' example, more suited to demonstrate Alfred Werner's looking over the fence to physics, was UV-vis spectroscopy (at Alfred Werner's time called spectral analysis (Spektralanalyse)), which he tried to implement as a structural characterization method of complexes in his group (Fox and Berke, 2014). Alfred Werner caught interest in this method in the range of 1912 – 1914, which at the time was known as a method for the spectral characterization of organic compounds and of inorganic solids only. But after 1914 Alfred Werner had stopped carrying out research with UV-vis spectroscopy. We do not know the real reason for that, but we can speculate that at the time UV-vis