

Gustav Magnus and his Green Salt

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When naming coordination compounds, early chemists were like the children of Israel, who called the food miraculously supplied to them in the wilderness *manna*, "for they wist not what it was" (*Exodus*, 16:15). Since the true constitutions and configurations of these compounds were unknown until the advent of Alfred Werner's coordination theory, complexes were often named after their colours (luteo, purpureo, roseo, praseo, violeo, etc.) or after their discoverers (Cleve's Salt, Erdmann's Salt, Fischer's Salt, Recoura's Sulphate, Reinecke's Salt, etc.). In 1897, Werner proposed a systematic nomenclature for cobalt-ammines based on his coordination theory, and this system is used today with only minor modifications.

One of the most famous and important coordination compounds named after its discoverer is tetraammineplatinum(II) tetrachloroplatinate(II), $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, Magnus' Green Salt, discovered in 1828 by Gustav Magnus, later Professor of Physics and Technology at the Universität Berlin (1).

Magnus' Life and Work

Heinrich Gustav Magnus is better known for his contributions to physics and technology than for those to chemistry (2). He was born in Berlin on May 2, 1802 and died there on April 4, 1870. Magnus' father,

Johann Matthias, the prosperous founder of a large trading firm, was able to provide his son with private instruction in mathematics and natural science. Gustav entered the Universität Berlin in 1822, and in 1825 he published his first paper, an investigation of pyrophoric iron, cobalt, and nickel (3) carried out under the direction of Eilhard Mitscherlich (1794-1863), discoverer of the law of isomorphism. Following his attainment of the doctorate in September 1827 with a dissertation on tellurium, Magnus took the advice of Mitscherlich, Heinrich Rose (1795-1864), Gustav Rose (1798-1873), and Friedrich Wöhler (1800-1882), all Berlin chemists who had studied with Jöns Jacob Berzelius (1779-1848), and in October 1827 went to Stockholm to study with the Master, who became his lifelong friend and adviser.

It was in Berzelius' laboratory that Magnus not only discovered the first platinum-ammine compound (Magnus' Green Salt,



Heinrich Gustav Magnus 1802-1870

Professor of Physics and Technology at the Universität Berlin, Magnus was mainly known as a physicist but he is best known to chemists for the discovery of the green salt that bears his name

The first page of Magnus' paper describing some compounds of platinum with chlorine, among which is tetraammineplatinum(II) tetrachloroplatinate(II), Magnus' Green Salt, the first platinum ammine complex to be discovered. The paper appeared in Volume 14 of *Annalen der Physik und Chemie* in 1828

[Pt(NH₃)₄][PtCl₄] and its related potassium salt (K₂[PtCl₄]) but also worked on the addition compound of ethylene and platinum chloride later described by the Danish chemist William Christoffer Zeise (1789–1847) (Zeise's Salt, K[Pt(C₂H₄)Cl₃]). In summer 1828, Magnus returned to Berlin where, with the exception of a visit to Gay-Lussac's laboratory in Paris during 1828 and 1829, he remained until his death. Magnus' *Habilitationschrift* on mineral analysis (1831) permitted him to begin lecturing on technology at the university and on chemistry at the Städtische Gewerbeschule but caused a break with his teacher Mitscherlich, who regarded the young Privat-Dozent as a dangerous competitor. In 1833 Magnus was appointed Ausserordentlicher (Extraordinarius) Professor and in 1845 Ordentlicher (Ordinarius) Professor of Technology and Physics at the Universität Berlin, where he also served as Rektor during 1861 and 1862. Magnus married Bertha Humblot in 1840. He became a member of the Berliner Akademie der Wissenschaften in 1840 and

was one of the organising members of the Deutsche Chemische Gesellschaft (founded in 1868). A number of his students (Wilhelm Beetz, Hermann Helmholtz, Gustav Wiedemann, Robert Schneider, John Tyndall, Rudolph Weber, and F. H. Adolph Wüllner) became famous physicists in their own right.

As was true of most chemists of the time, Magnus' research interests were varied. From an initial interest in mineral analysis, he turned to inorganic chemistry (discovered periodic acid and its salts in 1833) (4),

VIII. Ueber einige Verbindungen des Platinchlorürs; von G. Magnus.

Es sind bis jetzt zwei Verbindungen des Platins mit dem Chlor bekannt. Die eine, mit vier Atomen Chlor, das Platinchlorid, PtCl₄, erhält man, wenn Platin in Königswasser aufgelöst wird. Die andere mit zwei Atomen Chlor, das Platinchlorür, PtCl₂, bekommt man dagegen, wenn man das Chlorid bis zum Schmelzpunkt des Bleies erhitzt, wobei zwei Atome Chlor entweichen.

Das Chlorid bildet, wie bekannt, leicht Doppelsalze mit Chlorkalium, Chlornatrium, Chlorammonium, und wie Bonsdorff *) angiebt, auch mit andern Chlormetallen. Von diesen ist das Kaliumsalz, KCl + PtCl₄, neuerlich wiederum von Berzelius **) untersucht und zur Bestimmung des Platin-Atomgewichts, welches sich hiedurch = 1233,26 ergeben hat, benutzt worden.

Das Chlorür dagegen ist bis jetzt weniger bekannt gewesen, obgleich es ähnliche Doppelverbindungen wie das Chlorid bildet, von denen ich hier einige kurz beschreiben will.

Das reine Chlorür ist in Wasser unlöslich; wenn aber das Chlorid, aus welchem es dargestellt worden, nicht hinlänglich erhitzt gewesen ist; so löst sich der Rückstand mit einer so dunkelbraunen Farbe in Wasser, daß die klare Flüssigkeit völlig undurchsichtig erscheint. Diese Flüssigkeit ist eine Auflösung des Platinchlorürs in Platinchlorid. Dampft man dieselbe ab, so fällt ein braunes Pulver nieder, welches sich, wenn die Flüssigkeit abgegossen wird, nicht wieder in Wasser löst. Setzt man aber dem Wasser die abgegossene Flüssigkeit wie-

*) *Ann. de chim. et de phys.* XXXIX. p. 145., und dies. *Ann.* Bd. XI. S. 124.

**) *Dies. Ann.* Bd. XIII. S. 469.

organic chemistry (discovered ethionic acid, $\text{HSO}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, and isethionic acid, $\text{CH}_2\text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, in 1833–1839 (5); polymerisation of hydrocarbons on heating, 1853), physiological chemistry (oxygen and carbon dioxide content of blood, 1837–1845), and agricultural chemistry (1849). He gradually turned more and more to physico-chemical and eventually purely physical investigations, which constitute his most important scientific achievements. Among these we may cite his contributions to the theory of heat, thermal expansion of gases, transmission of heat through gases by conduction and radiation, diathermanity of gases, boiling of liquids, vapour formation, electrolysis (“Magnus’ Law”, which states that for each metal there is a specific voltage at which it is deposited from a solution containing a mixture of metallic salts (6)), induced and thermoelectric currents, optics, hydrodynamics, magnetism, and mechanics. Although Magnus’ main claim to fame was as a physicist, he never ceased to work on chemical problems in his private laboratory. These later chemical works, however, never matured to results of general significance; they served merely for his own instruction.

Gustav Magnus was neither a theoretician nor an original thinker. The objects of his work had almost all been investigated by other scientists. He was, however, an acute, conscientious, and diligent experimenter, who uncovered much valuable physical and chemical data. He is best known to chemists for his discovery of the important green salt that bears his name.

Magnus’ Salt

As the first discovered platinum-ammine, Magnus’ salt is numbered among the earliest known coordination compounds. It is of course true that the corresponding pink palladium compound, tetraamminepalladium(II) tetrachloropalladate(II), $[\text{Pd}(\text{NH}_3)_4][\text{PdCl}_4]$ (Vauquelin’s Salt), was discovered fifteen years earlier, but Magnus’ salt has played a much more significant role in the develop-

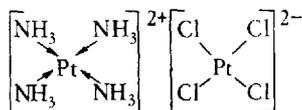
ment of coordination chemistry because of the great stability and retention of configuration characteristic of platinum compounds. Magnus’ salt later served as the starting point for a great amount of research on the so-called platinum bases carried out by chemists such as Gros, Reiset, Peyrone, Raewsky, Gerhardt, Cleve, and many others. It is still a valuable intermediate and useful reagent for the preparation of a wide variety of platinum complexes.

Magnus added excess aqueous ammonia to a solution of platinum(II) chloride in hydrochloric acid, whereupon a green, insoluble salt was slowly deposited. With the formation of this precipitate, Magnus simultaneously discovered both the most important cation ($[\text{Pt}(\text{NH}_3)_4]^{2+}$) and the most important anion ($[\text{PtCl}_4]^{2-}$) of divalent platinum. More convenient, alternative syntheses have since been devised (7). Magnus also described the preparation of the tetrachloroplatinates of potassium, ammonium, and sodium (8), and most of his short but historic article (1) is devoted to these compounds.

Magnus’ Green Salt has the same empirical formula as several other platinum(II)-ammine compounds, viz., *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (Peyrone’s Chloride), *trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (Reiset’s Second Chloride), $[\text{Pt}(\text{NH}_3)_3\text{Cl}][\text{Pt}(\text{NH}_3)\text{Cl}_3]$, $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{NH}_3)\text{Cl}_3]_2$, and $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2[\text{PtCl}_4]$. The series constitutes a classic example of what Werner has called “coordination polymerism” (*Koordinationspolymerie*), a type of structural isomerism in which the isomers have the same composition but formula weights that are different multiples of the same formula weight. The last compound in the series is believed to be one of the constituents of a so-called red modification of Magnus’ Green Salt with almost identical physical and chemical properties, discovered by Jørgensen and Sørensen and subsequently investigated by others. Peyrone (7b) was first to formulate Magnus’ Green Salt correctly as $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$.

The fact that Magnus’ Green Salt differs markedly in colour from its constituent ions

($[\text{Pt}(\text{NH}_3)_4]^{2+}$, colourless; $[\text{PtCl}_4]^{2-}$, orange-red) indicates considerable interaction between the cationic metal atom and anionic metal atom, and consequently its crystal structure and related properties have been extensively investigated (9). The salt is perhaps the simplest prototype of a large class of d^8 metal complexes exhibiting short metal-metal spacings (9c). The absorption spectra (9b) and electronic spectra (10) differ greatly from those of its constituent ions. The crystal structures of its cation (11) and anion (12) have both been determined, and in each case the central platinum atom has been found to be surrounded by four ammonia molecules or four chlorine atoms, respectively, in the square planar arrangement predicted by Werner:



In the crystal these cations and anions are stacked with parallel planes forming continuous chains of metal atoms.

In 1966 Collman (13) suggested that single crystals of transition metal complexes with linear chains of metal atoms might behave as anisotropic metallic conductors. Single crystals of Magnus' Green Salt have been found to exhibit anisotropic semiconductor properties and photoconduction with the highest conduction in the direction of the metal-metal chain, indications of considerable direct metal-metal interaction (14). The unusual solid state properties associated with this unusual compound will undoubtedly make it an object of even more experimental and theoretical studies in the future.

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