

Michele Peyrone (1813–1883), Discoverer of Cisplatin

doi:10.1595/147106710X534326

<http://www.platinummetalsreview.com/>

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The Italian chemist Michele Peyrone (1813–1883) was the first to synthesise cisplatin (cis-diamminedichloroplatinum (II)), the basis of today's most widely used family of anticancer drugs. This biographical article aims to present, for the first time in the English language, a summary of his life and the achievements that he made during his scientific career. Originally trained in medicine, Peyrone moved to chemistry and attended some of the most prestigious institutions in Europe in his time. He wrote several publications describing his work on 'Peyrone's chloride' ($\text{PtCl}_2(\text{NH}_3)_2$) and Magnus' green salt ($[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$). He later turned his attention to agricultural science where he defended important advances in the understanding of plant growth. Michele Peyrone's dedication to science is best summarised in the English translation of his first report on the synthesis of cisplatin: "I am determined to pursue this subject with all my energies, without having regard for the difficulties to be encountered at every step in so expensive and delicate a research".

In this age of high-throughput drug discovery, medicinal chemistry and targeted therapies, there are few clinically used anticancer drugs that were synthesised 130 years before their biological activity was discovered. An alert reader will immediately think of the arsenal of natural products that have found application in the clinic in recent years, but even these have been semi-synthetically modified following their discoveries. By contrast, one of the most widely used anticancer drugs today, cis-diamminedichloroplatinum (II) or cisplatin, originally known as Peyrone's chloride, was first prepared in its presently used form by Italian chemist Michele Peyrone in 1844 (1). It later played a central role in the Nobel prize-winning work of Swiss chemist Alfred Werner (1866–1919) (2, 3) on isomerism in inorganic complexes. The cytostatic activity of cisplatin was first reported by Barnett (Barney) Rosenberg (1926–2009) and coworkers in 1965 (4), and it progressed rapidly into the clinic (5). Many publications concerning

cisplatin mention its discoverer, Michele Peyrone, but no English language biography exists of the man who first prepared what is now a billion-dollar drug. This article aims to remedy this gap in the scientific literature with a relatively brief summary of Peyrone's life, career, positions, achievements and honours. His work on platinum compounds is introduced here, and will be discussed in more detail in a forthcoming article in this Journal.

NB: Translations given in square brackets in this article are by the present authors.

Early Life

Michele Peyrone (6–8) (Figure 1), the son of Vittorio and Teresa Peyrone (née Bonino), was born on 26th May 1813 in Mondovì Breo, a small village originally separate but now part of Mondovì, a town about 60 miles south of Turin, Italy. He was to spend much of his professional life in this region of Piedmont in northern Italy, which was then part of the Kingdom of Sardinia, governed by the Casa Savoia [House of Savoy]. His family was apparently quite wealthy, and as a result Michele was financially comfortable throughout his entire life. However, his parents died when he was young, and he entered school relatively late because of poor health. Michele attended the gymnasium (a secondary school that prepares students for higher education) in the small town of Brà,

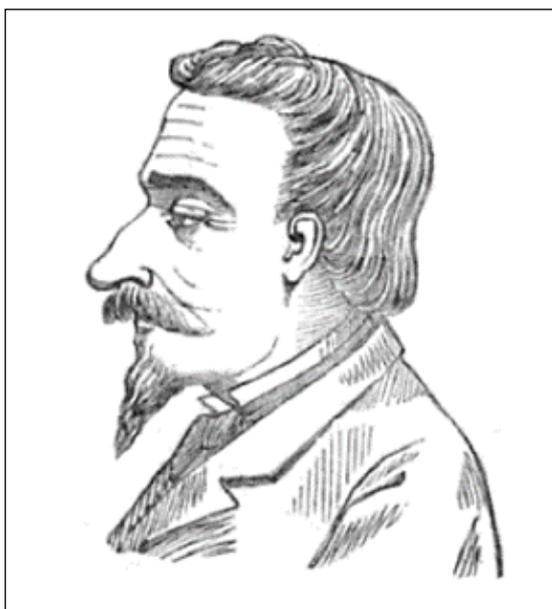


Fig. 1. Michele Peyrone (1813–1883) (7)

about 50 km (31 miles) south of Turin. He then moved to Turin, which was the capital of the Kingdom of Sardinia, to attend the Università di Torino, intending to become a lawyer, but after a few months he changed faculties and earned his Doctor of Medicine degree on 10th June 1835. In that year a cholera epidemic erupted in Europe, and Peyrone was assigned to treat patients at the cholera hospital in Mondovì, an unenviable task. During the next few years he travelled throughout Italy visiting hospitals and universities, although few details about this time are available.

Studies with Dumas

After visiting the leading Italian hospitals and universities, Peyrone decided to abandon medicine and devote himself to chemistry. In 1839 he moved to Paris to study physiological chemistry under the famous French chemist Jean Baptiste André Dumas (1800–1884) (9) at the École Polytechnique, founded in 1794 and at that time one of the world's most prestigious universities. In the Faculty of Science he probably met fellow Italian chemist Raffaele Piria (1814–1865) (10). At the time of Peyrone's arrival Dumas was already well known for a number of scientific discoveries. Furthermore, in 1832 Dumas became the first chemist in France to introduce practical laboratory training (11), perhaps inspired by his own apprenticeship with an apothecary. Although Peyrone did not produce any self-authored published work during his time in Dumas' laboratory, Dumas published an essay on the physiology of plants and animals that drew correlations between plant and animal metabolism (12) and was beginning research in his laboratory on what ultimately became Peyrone's primary field – agricultural chemistry.

Years at Gießen and Initial Research on Platinum Compounds

In 1842 Peyrone moved from Dumas' laboratory in Paris to work with Dumas' scientific nemesis, Justus von Liebig (1803–1873) (13), at the Universität Gießen (an institution that now bears Liebig's name) in the state of Hesse in central Germany. This was the most important period for Peyrone's scientific work, and he and Liebig remained close friends until the latter's death three decades later. Liebig, who is generally credited with originating the modern research laboratory, was also strongly interested in agricultural chemistry and physiology (14), and he

had a number of scientific disputes with Dumas during this time, when Peyrone travelled across Europe from one laboratory to the other.

It was at Gießen between 1842 and 1844 that Peyrone initiated his research on platinum compounds. Here he investigated Magnus' green salt, $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ (which can be described by the formula $\text{PtCl}_2(\text{NH}_3)_2$) (15) (Figure 2(a)), the first discovered platinum-ammine salt, prepared in 1828 by German physicist and chemist Heinrich Gustav Magnus (1802–1870) (16) while working in the Stockholm laboratory of Swedish chemist Jöns Jacob Berzelius (1779–1848) (17). Peyrone intended to continue experiments with Magnus' green salt and to examine its reactivity, based on the preceding work of James Gros (also from Liebig's laboratory) and Jules Reiset (1818–1896). However, when attempting to synthesise Magnus' green salt by adding excess ammonia to an acidified PtCl_2 solution, Peyrone noted the appearance of two products – one green (Magnus' green salt) and one yellow. He separated the two on the basis of the insolubility of Magnus' green salt in hydrochloric acid. The filtrate yielded a yellow precipitate ($\text{PtCl}_2(\text{NH}_3)_2$), isomeric with Magnus' green salt ($[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$), but with entirely different properties (Figure 2(b)).

Peyrone reported his work in 1844 in *Annalen der Chemie* (in German), the journal founded by his mentor, Liebig (1a). That same year it was also reported in French in *Annales de Chimie*, his previous mentor Dumas' journal (1b), and summarised in English (at Peyrone's request) by the Irish chemist James Sheridan Muspratt (1821–1871), who was working in Liebig's laboratory at the time (1c).

Peyrone had difficulties in interpreting his results, and near the end of his article he admitted that he was uncertain about the difference between his new compound and Magnus' green salt. He refused to

recognise the word isomerism, which he considered “*ein leerer Name*” [an empty name]. He supposed that his yellow ‘salt’ was the product of the first combination between ammonia and PtCl_2 and that Magnus' green salt was the second one.

European Travels and Final Research on Platinum Compounds

In 1844 Peyrone departed from Gießen because of poor health. He then travelled through Germany, Holland, Belgium and England to visit laboratories, chemical industries and hospitals. He was proud of his linguistic abilities: in addition to Italian, he was proficient in Latin, French, English and German. After this, he returned to Turin, where he became an assistant in the chemical laboratory directed by G. L. Cantù and continued his research.

In a duplicate report of 1845 (18) Peyrone described the same compounds with the same composition but different chemical and physical properties that he had reported in 1844 (1), along with some additional information. Here he uses the term ‘isomerism’, which he had earlier disdained:

“*Dieß ist ein Beispiel von Isomerie, dem man nur bei sehr wenigen organischen Verbindungen begegnet*” [This is an example of isomerism, which is encountered only among a very few organic compounds] (18).

He expressed the same view in an Italian article of 1847 (19), in which he studied the action of ammonium sulfite on the isomers of Magnus' green salt. It is important to note that Peyrone did not assign the *cis* isomeric structure to his chloride; this did not become possible until Werner's work some 60 years later (20).

In his final article on platinum compounds (21) Peyrone reported the action of nitric acid on Magnus'

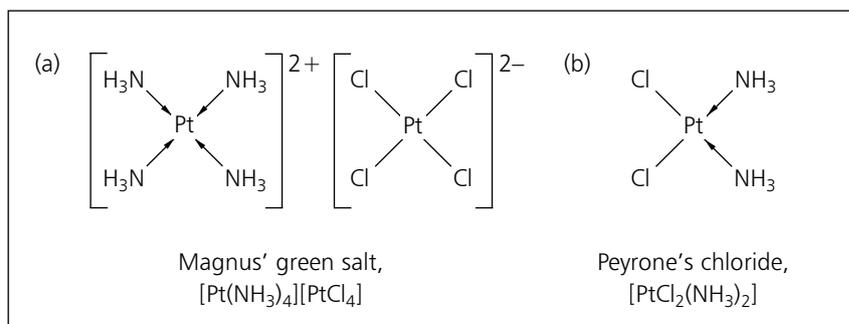


Fig. 2. Modern chemical structures of the isomers, Magnus' green salt (green) and Peyrone's chloride (yellow), both of which can be described by the formula $\text{PtCl}_2(\text{NH}_3)_2$ (1)

green salt, which produced Gros' nitrate (*trans*-[PtCl₂(NH₃)₄](NO₃)₂). Reaction of nitric acid with his other compounds resulted in entirely different products.

Agricultural Science

While Peyrone was initiating his work on platinum in Liebig's laboratory, a momentous debate was raging in Europe on Liebig's theories of agricultural science (14). Liebig had rejected the contemporary theory that plants absorb carbon from humus in the ground, and he seemed to prove this by showing that some crops actually enrich the soil's carbon content. He examined the minerals formed on burnt plants and proposed that plants absorbed ammonia and other nutrients from the soil. He further hypothesised that nitrogen and minerals could stimulate plant growth, and, after several unsuccessful experiments, by about 1850 he demonstrated this to be the case, thus founding the concept of fertilisers that revolutionised agrarian practices. The Italian obituaries of Peyrone (6–8) cite his ardent defence of Liebig's theories, and when Peyrone returned to Italy, it was agricultural science that became his primary field of study.

Genoa and Turin

After Peyrone spent several months in Turin, the Piedmont government appointed him to teach applied chemistry at the Genova Scuola Serale di Arti Applicate [Genoa Evening School of Applied Arts]. Here he delivered his initial plenary lecture on 20th November 1847 (22). In 1849 he was appointed Professor at the Università di Genova. While in Genoa, Peyrone completed his platinum studies, and with Professor Tullio Brugnatelli (1825–1906) he reported on the analysis of four mineral waters from the nearby area of Valdieri (23). By a Royal Act of 23rd October 1854, Peyrone was moved to Turin, where he was appointed Professor of Applied Chemistry at the Reale Istituto Tecnico [Royal Technical Institute]. Liebig's influence on Peyrone also began to emerge, as he was then appointed Professor of Agricultural Chemistry at the Università di Turino with teaching responsibilities. Later he was entrusted for two years with the teaching of organic chemistry with applications to physiology.

Shortly after his return to Turin, in 1855 Peyrone married Ester Daziano. After only three years of marriage, his wife died, leaving him with two daughters, Ida (born 15th May 1856) and Ester (born 14th

October 1858). Peyrone continued to advance professionally, being nominated Professor of General Chemistry and Vice Director of the laboratory at the Università di Turino. He also delivered a free course in Agricultural Chemistry from 1860 to 1866, based on the guidelines of the well-known book written by his former mentor Liebig in 1840 (14). Peyrone's course evolved into a book, the first part of which appeared in 1869 (24a) (Figure 3) and the second, in 1871 (24b). It dealt with the history of agriculture from 1840 and emphasised soils as well as modern advances in plant physiology and its implications for agriculture (25). Peyrone's death prevented the appearance of a planned third volume (7).

During these years, along with his teaching of agricultural chemistry, Peyrone authored a series of publications on various topics in agriculture, including the requirements for plant growth (26), an introduction to his agricultural chemistry course (27), the causes of the souring of wine (28), rural production (29), and other topics (30–33).

In 1866 Peyrone resigned his position as Professor at the Università di Turino (apparently due to disputes

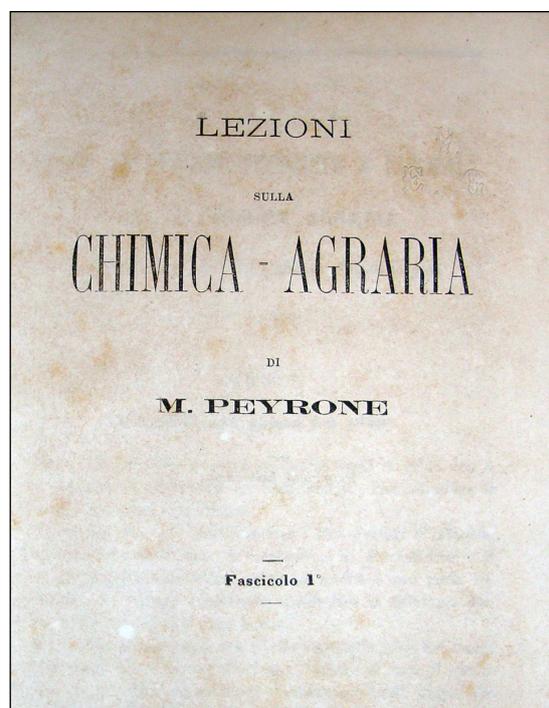


Fig. 3. Cover page of Michele Peyrone's work, "Lezioni sulla chimica agraria" [Lessons on agricultural chemistry], Part 1 (24a) (Photograph by Matthew D. Hall)

over the politics of promotion) and returned to teaching at the Reale Istituto Tecnico in Turin, which in the meantime had merged with the Reale Museo Industriale [Royal Museum of Industry], also in Turin, an institution founded in 1862 to promote industrial education and the advancement of industry and commerce and of which Peyrone was Chairman. However, in 1867 the two institutions were divided again, and although Peyrone requested that he be attached to the Museo, he was instead assigned to the Istituto Tecnico, which was not a university.

Positions and Miscellaneous Honours

From 1856 to his retirement Peyrone was appointed a member of the Reale Accademia di Agricoltura [Royal Academy of Agriculture] in Turin, of the Accademia Medico-Chirurgica [Academy of Medicine and Surgery] in Genoa, of the Società Economico-Agraria [Society of Agrarian Economics] in Perugia, of the Società Farmaceutica [Pharmaceutical Society] of Sardinia, and of the Comizio Agrario [Chamber of Agricultural Rally] in Mondovì, his birthplace. He was named Cavaliere dell'Ordine Mauriziano [Knight of the Order of St. Maurice] and Commendatore della Corona d'Italia [Knight Commander of the Crown of Italy]. During the Crimean War (1854–1856) he was appointed Superintendent for Food of the Piedmontese Army, and as a chemist he was appointed by the recently unified Italy's first Prime Minister, Count Camillo Benso di Cavour (1810–1861), to a committee established to study agricultural problems and the use of artificial fertilisers.

Final Years

As time went on Peyrone became worn out and fatigued. Even during his childhood he had been unwell, and he apparently had never recovered from the loss of his wife in about 1858 and the premature death of his daughter Ester at the age of 13 (probably in about 1870). In 1879 he was placed on leave for health reasons, and he ultimately retired that same year. He moved to the small town of Magliano Alpi close to Mondovì and then to nearby Carrù, where his daughter Ida had married the mayor, G. B. Reyneri. In retirement Peyrone apparently devoted himself exclusively to the care of his 'estates' and to the quiet country life. He died at Carrù with his family at his side in July 1883, at the age of 70. Details regarding his funeral, burial or grave have not been found.

Concluding Remarks

Obituaries of Peyrone (6–8) testify to the important contributions that he had made to chemistry. Although he was well known for his work on agricultural chemistry, his early work on platinum was also mentioned, demonstrating that the importance of this work was well recognised. Vincenzo Fino described him as “independent, of a frank and severe character” – perhaps the qualities needed to travel throughout Europe, succeed in the relatively solitary pursuit of research, and defend Liebig's principles of agricultural science in Italy (6). Peyrone apparently recognised his responsibility as a man born into wealth and often stated, “the duty of the rich is to help the poor” (6).

Perhaps Michele Peyrone's dedication to science is best summarised by quoting from the English translation of his first report on the synthesis of cisplatin (1c):

“I am determined to pursue this subject with all my energies, without having regard for the difficulties to be encountered at every step in so expensive and delicate a research”.

We will examine Peyrone's work on platinum compounds in detail in a forthcoming article in *Platinum Metals Review*.

Acknowledgements

This research was partly supported by the Intramural Research Program of the National Cancer Institute, National Institutes of Health, Bethesda, Maryland, USA.

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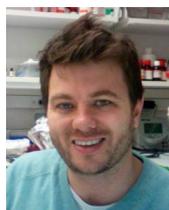
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Sandro Doldi (1908–2001) was a chemist, researcher and industrial and university professor who believed that research should attain results useful for all humanity. He achieved national and international recognition for his studies of water in all its aspects. His teaching served as a model for the mastery of theoretical and practical knowledge rarely seen in a single scholar. In his "Ricordi di un tecnico" (Edizione Portalupi, Casale Monferrato, 2002) he described the long path of his daily life as an indefatigable scholar and researcher, interspersing the episodes of his personal life with Italian history.



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