Alfonso Cossa

THE MAN AND HIS PLATINUM SALTS

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Almost every co-ordination chemist or platinum chemist is familiar with Cossa's first and second salts, $K[PtCl_3(NH_3)].H_2O$ and $K[PtCl_5(NH_3)].H_2O$, respectively, yet the life and work of their discoverer is virtually unknown outside of Italy. Cossa made outstanding contributions not only to the chemistry of platinum and to inorganic chemistry in general, but also to agricultural and plant chemistry, mineralogy, petrography, medicine, botany, forensic chemistry, and the analysis of soils and rocks, especially those of his native land.

Alfonso Cossa was born in Milan, Italy on November 3, 1833, the son of Giuseppe Cossa, librarian of Milan's famous Biblioteca di Brera and an authority on paleography and diplomacy, and his wife Maria. He completed his classical studies in Milan and in 1852 went to Pavia, an ancient town 20 miles south of Milan known as the Oxford of Italy because of its many colleges (1–5). Here he studied at the Collegio Borromeo, and in November, 1857 he received the degree of Doctor of Medicine from the Università di Pavia with a dissertation on the history of electrochemistry (6). Even before receiving his degree Cossa, at the early age of 23, had translated into Italian two of Justus Liebig's books "Die Grundsätze der Agricultur-Chemie mit Rücksicht auf die in England angestellten Untersuchungen" (The Principles of Agricultural Chemistry with Reference to the Investigations Instituted in England) (1855) (7) and "Über Theorie und Praxis in der Landwirtschaft" (On Theory and Practice in Agriculture) (1856) (8).

Cossa was that rare type of scholar who with the passing years enters fields of knowledge in which he did not have formal training. After his education as a physician, he became successively a botanist, an agricultural chemist, a mineralogical chemist, and an inorganic and co-ordination chemist. When his favourite branch

Alfonso Cossa
1833–1902

Born in Milan, Cossa had an illustrious career as a chemist and lithologist. He founded, published and edited, from 1872 to 1882 the journal, *Le Stazioni sperimentali agrarie italiane*. He was President of the Turin Academy of Sciences and for some fifteen years was Director of the Reale Scuola di Applicazione degli Ingegneri di Torino. He died in Turin

of chemistry, mineralogical chemistry, underwent many changes as a result of new physicochemical theories, Cossa, although a mature scholar with a substantial reputation, returned to school to learn the mathematical ideas now essential to modern chemistry. This continual evolution of his intellectual development characterised him throughout his life.

From an early age Cossa was interested in chemistry, especially applied chemistry. He had unusual scientific and didactic talents, but at the beginning of his career he was forced to learn much completely by himself. In an autobiographical letter to the chemist Arcangelo Scacchi, Cossa admitted:

> "Concluding my confession by telling you that the little that I have done, I have done by myself with the firm will to overcome the obstacles that presented themselves to me at every step"(2).

The state of science and chemistry in Italy during the decade 1850–1860 forced Cossa to study chemistry by himself, initiating research that had only an indirect relationship to chemistry and later becoming a good self-taught scholar. At this time, Dumas, Laurent, Gerhardt, Cahours, Wurtz, Berthelot and Saint-Claire Deville were active in France; Germany had Liebig, Wöhler, Bunsen, Kolbe, Hofmann, Strecker and Kekulé; and England had Graham, Williamson, Frankland and Odling. Excluding Faustino Malaguti (1802–1878), who had fled to Paris in 1831 as a political refugee, the only notable chemists in Italy were Rafaelle Piria (1815–1865), Francesco Selmi (1817–1881) and Ascanio Sobrero (1812–1888), and of these only Piria occupied a university chair. Furthermore, none of these chemists established a school; they each worked on their own and had very few students. In the words of Icilio Guareschi "they were like bright points in a dark night" (2).

At that time most university positions were occupied by men whose teaching was purely theoretical and who failed to consider the great progress in chemistry being made in other countries. Indeed, the teaching of chemistry in Italy was comparable to that existing in other countries sixty years earlier.

Like the government of the Papal States, the absolute governments that existed in the Piedmonte region of north-western Italy before the 1848 revolution and in the rest of Italy before 1859 not only failed to promote scientific progress but actually discouraged it. Thus, during the eighteenth century and the first half of the nineteenth century, great scientists born in Italy such as Joseph Louis Lagrange, Pellegrino Rossi, Macedonio Melloni and Faustino Malaguti deserted their native land for other countries because of uncaring governments, political reasons or lack of means for study.

Cossa confessed that in 1858 he did not know where to go to study chemistry. In an 1893 lecture he recalled:

> "the idea of collecting information on the life and works of Angelo Sala arose in me a long time ago, going back to the year 1858. Fond of chemistry but compelled to a platonic love because at that time at the Università di Pavia young students were not allowed to dedicate themselves to experimental researches in a laboratory, I tried to satisfy my inclination by applying myself, as I knew and was able, to the study of the history of science."

There was a great shortage of teachers in Italy at the time that Cossa received his medical degree, so he remained at the Università di Pavia, becoming professore di chimica and direttore of the Istituto Tecnico in 1861. His outstanding qualities as a researcher and teacher were recognised by Quintino Sella (1827–1884), the statesman and crystallographer who helped place the new national government on a firm footing after Italy's unification. Thus when Venice was united to the newly formed kingdom of Italy in 1866, Sella commissioned Cossa to organise and found in Udine, an Istituto Tecnico, where he remained until 1872 as professore di chimica and direttore.

After a short stay (1872–1873) in the Reale Scuola Superiore di Agricoltura at Portici, in 1873 Cossa was appointed direttore of the Stazione Agraria and insegnante di chimica mineraria at the Reale Museo Industriale, both in Turin. In 1882 he succeeded Ascanio Sobrero, the discoverer of nitroglycerin, as professore di chimica docimastica e mineraria at

Turin's Reale Scuola di Applicazione degli Ingegneri di Torino, of which in 1887 he became direttore, a post that he retained until his death on October 23, 1902 after a short illness.

Cossa's Early Research

The subject of Cossa's early works was largely agricultural and plant chemistry. His first research paper dealt with absorption by roots (10), and much of his work concerned the chemistry of plant seeds, soils, water supplies, manures, sugar beet roots, the must of grapes, the ash of the leaves and fruit of lemon trees and asparagine in vetches, some of which work overlapped his mineralogical studies.

Throughout his career mineralogical chemistry was Cossa's primary field of interest, with almost half of his works being devoted to this subject, from his first mineralogical work, published in 1869 (11), to his last, published thirty years later in 1899 (12). He classified, characterised the properties of, determined the compositions of and proposed mineralogical formulae for dozens of minerals and rocks from many sources. One of the minerals that he studied, a variety of paragonite—a sodium mica of composition $H_2NaAl_3(SiO_4)_3$— was named cossaite in his honour. Cossa analysed minerals and rocks of Vulcano in the Lipari Isles, and in the stalactiform concretions in the Vulcano crater he discovered and analysed a new mineral of composition K_2SiF_6, which he named hieratite (13). Cossa also analysed cinders and lava from the eruption of Mount Etna on June 28th and July 2nd, 1879 (14).

A number of Cossa's petrographic and mineralogical works on Italian rocks and minerals were published in a 304-page volume in 1881 (15). The collection of thousands of these specimens ordered and classified by Cossa is now housed in the Politecnico di Torino.

Closely related to his mineralogical studies were Cossa's investigations of several lanthanides or rare earths, namely, lanthanum, cerium and didymium (a supposed rare earth element discovered by Carl Gustav Mosander in 1841, but subsequently separated into neodymium and praseodymium in 1887 by Carl Auer, Baron von Welsbach). Cossa found these elements to be widely distributed in nature (16). He assumed that the association of three rare earth elements, yttrium (17), cerium (17) and didymium (18) with calcium in various minerals supported his supposition that these elements are dipositive, as did his preparation and characterisation of cerium molybdate (19) and didymium molybdate (20).

Platinum-Ammines

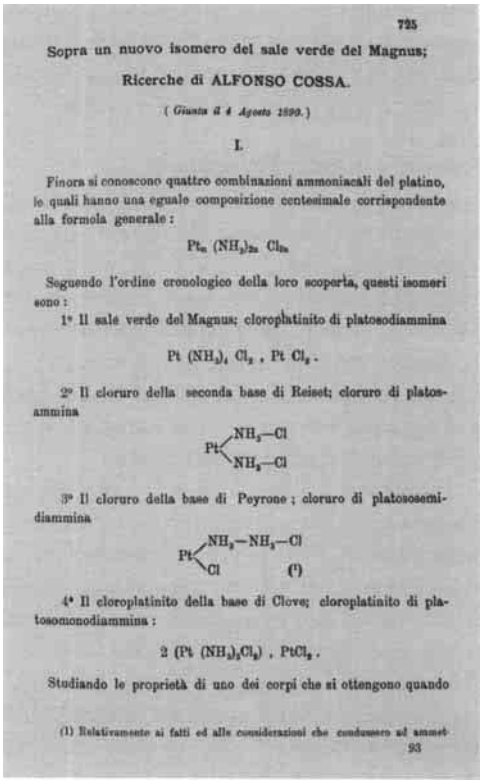
Long interested in biography and the history of chemistry, Cossa wrote articles on the life and work of a number of chemists, one of which led him to undertake a new field of research, the platinum-ammines.

Cossa's First Salt, $K[PtCl_3(NH_3)].H_2O$

In 1885 the Accademia dei Lincei asked Cossa to commemorate the life and work of his friend Quintino Sella (21), who had died the previous year. In the course of his bibliographical research, Cossa encountered Sella's "Sulle forme di alcuni sali di platino a base di platinodiamina" published in 1856–1857 (22), and he decided to carry out experimental studies on platinum-ammine compounds. Beginning on May 3, 1885 (23) and continuing until 1897, he made a long series of investigations—his most important chemical contributions. At this late stage of his career, he was fortunate to have the Ministero della Pubblica Istruzione and the direttore of the Reale Museo Industriale Italiano di Torino furnish sufficient funds for him to procure a half-kilogram of metallic platinum from Kahlbaum in Berlin. He also had at his disposal the excellent equipment and facilities of the Stazione Agraria di Torino, equalled by few university laboratories in Italy.

One of the most famous and important coordination compounds to be named after its discoverer is Magnus' green salt, tetraammineplatinum(II) tetrachloroplatinate(II), $[Pt(NH_3)_4][PtCl_4]$, discovered in 1828 (24) in Berzelius' laboratory by Heinrich Gustav Magnus (1802–1870) (25). As the first

The first page of Cossa's article published in 1890 entitled "On a New Isomer of Magnus' Green Salt", *Gazz. chim. ital.*, 1890, 20, 725, in which Cossa discusses platinum-ammines



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Sopra un nuovo isomero del sale verde del Magnus;

Ricerche di ALFONSO COSSA.

(*Giunta il 4 Agosto 1890.*)

I.

Finora si conoscono quattro combinazioni ammoniacali del platino, le quali hanno una eguale composizione centesimale corrispondente alla formola generale:

$$Pt_m (NH_3)_{2n} Cl_{2n}$$

Seguendo l'ordine cronologico della loro scoperta, questi isomeri sono:

1° Il sale verde del Magnus; cloroplatinito di platosodiammina

$$Pt (NH_3)_4 Cl_2 , Pt Cl_4 .$$

2° Il cloruro della seconda base di Reiset; cloruro di platosammina

3° Il cloruro della base di Peyrone; cloruro di platosodiammina

(1)

4° Il cloroplatinito della base di Cleve; cloroplatinito di platosomonodiammina:

$$2 (Pt (NH_3)_2Cl_2) , PtCl_4 .$$

Studiando le proprietà di uno dei corpi che si ottengono quando

(1) Relativamente ai fatti ed alle considerazioni che condussero ad ammet-

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discovered platinum-ammine, it is among the earliest known co-ordination compounds and played a significant role in the history of co-ordination chemistry because of the great stability and retention of the configuration characteristic of platinum compounds. It served as the starting point for a vast amount of research on the so-called platinum bases, not only by Cossa but also by Gros, Reiset, Peyrone, Raewsky, Gerhardt, Cleve and many other chemists. Its constituent cation and anion are the most important ions of dipositive platinum. It has the same empirical formula as five other platinum(II) compounds, namely *cis*-$[PtCl_2(NH_3)_2]$ (Peyrone's chloride) (26, 27), *trans*-$[PtCl_2(NH_3)_2]$ (Reiset's second chloride) (27, 28), $[PtCl(NH_3)_3][PtCl_3(NH_3)]$ (29), $[PtCl(NH_3)_3]_2[PtCl_4]$ (30) and $[Pt(NH_3)_4][PtCl_3(NH_3)]_2$ (31). The last compound was discovered by Cossa. This series is a classic example of what Alfred Werner called Koordinationspolymerie (co-ordination polymerism) (32, 33), 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.

Before the advent of Werner's co-ordination theory in 1893 (34), theories of the constitution of so-called complex compounds were advanced by Thomas Graham (1837), Jöns Jacob Berzelius (1841), Jules Reiset (1844), Charles Frédéric Gerhardt (1850), August Wilhelm von Hofmann (1851), Carl Ernst Claus (1856) and August Kekulé (1864) and most successfully by Christian Wilhelm Blomstrand's chain theory (1869) as subsequently modified and developed by Sophus Mads Jørgensen (35). Although Cossa interpreted his data in terms of the now obsolete Blomstrand-Jørgensen chain theory (36) and named his compounds according to Cleve's obsolete nomenclature system (37), his experimental results are in no way invalidated.

In attempting to reconcile some discrepancies between the work of Reiset (28) and Cleve (39), Cossa treated solutions of tetraammineplatinum(II) chloride and sodium hexachloroplatinate(IV) in stoichiometric amounts at 0°C and obtained a precipitate of yellow amorphous tetraammineplatinum(II) hexachloroplatinate(IV) (23, 39). He established the constitution of this substance by treating its solution with one of potassium

tetrachloroplatinate(II), whereupon the well-characterised Magnus' green salt and potassium hexachloroplatinate(IV) were formed:

$$Pt(NH_3)_4Cl_2,PtCl_4 + (KCl)_2,PtCl_2 \rightarrow Pt(NH_3)_4Cl_2,PtCl_2 + (KCl)_2,PtCl_4,$$ that is,

$$[Pt(NH_3)_4][PtCl_6] + K_2[PtCl_4] \rightarrow [Pt(NH_3)_4][PtCl_4] + K_2[PtCl_6]$$ (modern).

Continuing his work, Cossa discovered a fifth isomer of Magnus' green salt, in addition to the four isomers already known. By treating Magnus' green salt with a boiling solution of ammonium nitrate, he obtained a mixture of *trans*-$[PtCl_2(NH_3)_2]$ (platosammine chloride), *trans*-$[PtCl_2(NH_3)_4](NO_3)_2$ (platinodiammine chloronitrate), and the new yellow isomer, $[Pt(NH_3)_4][PtCl_3(NH_3)]_2$, which he regarded as a compound of one molecule of platosodiammine chloride ($Pt(NH_3)_4Cl_2$, modern $[Pt(NH_3)_4]Cl_2$) and two molecules of the chloride of a new base, which he called platosemiammine ($PtCl.NH_3Cl$) (31, 40). He thus formulated the compound as $2\begin{pmatrix}NH_3Cl\\Cl\end{pmatrix},Pt(NH_3)_4Cl_2$. The orange-red "potassiochloride" of this new base, now known as Cossa's first salt, $K[PtCl_3(NH_3)].H_2O$, is readily soluble in water and yields the new isomer of Magnus' green salt on treatment with platosodiammine chloride:

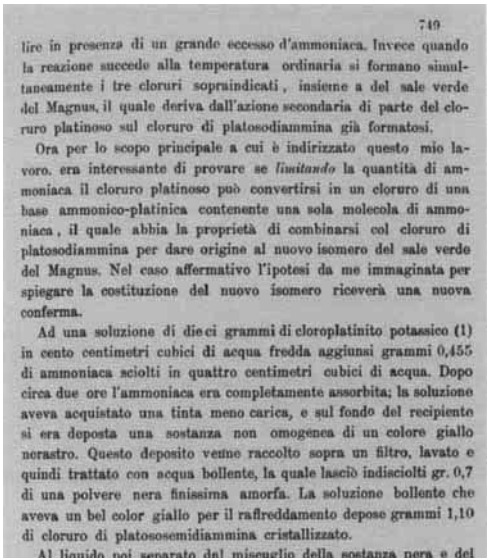
$$2(Pt(NH_3)Cl_2,KCl) + Pt(NH_3)_4Cl_2 \rightarrow 2Pt(NH_3)Cl_2,Pt(NH_3)_4Cl_2 + 2KCl,$$ that is,

$$2K[PtCl_3(NH_3)] + [Pt(NH_3)_4]Cl_2 \rightarrow [Pt(NH_3)_4][PtCl_3(NH_3)]_2 + 2KCl$$ (modern).

Cossa's Second Salt, $K[PtCl_5(NH_3)].H_2O$

By oxidising $K[PtCl_3(NH_3)].H_2O$ (Cossa's first salt) in aqueous solution with either chlorine or potassium permanganate, Cossa obtained the corresponding yellow platinum(IV) salt, $K[PtCl_5(NH_3)].H_2O$, now known as Cossa's second salt, which he called platinosemiammine potassium chloride and formulated as $Pt(NH_3)Cl_4,KCl$ (31). In solution treatment of this compound with $[Pt(NH_3)_4]Cl_2$ produced a vermilion-red precipitate of unstable $[Pt(NH_3)_4][PtCl_5(NH_3)]_2$ (31).

Cossa confirmed his view that one atom of platinum(II) could combine with one molecule of a base to form compounds analogous to his



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lire in presenza di un grande eccesso d'ammoniaca. Invece quando la reazione succede alla temperatura ordinaria si formano simultaneamente i tre cloruri sopraindicati, insieme a del sale verde del Magnus, il quale deriva dall'azione secondaria di parte del cloruro platinoso sul cloruro di platosodiammina già formatosi.

Ora per lo scopo principale a cui è indirizzato questo mio lavoro, era interessante di provare se *limitando* la quantità di ammoniaca il cloruro platinoso può convertirsi in un cloruro di una base ammonico-platinica contenente una sola molecola di ammoniaca, il quale abbia la proprietà di combinarsi col cloruro di platosodiammina per dare origine al nuovo isomero del sale verde del Magnus. Nel caso affermativo l'ipotesi da me immaginata per spiegare la costituzione del nuovo isomero riceverà una nuova conferma.

Ad una soluzione di dieci grammi di cloroplatinito potassico (1) in cento centimetri cubici di acqua fredda aggiunsi grammi 0,455 di ammoniaca sciolti in quattro centimetri cubici di acqua. Dopo circa due ore l'ammoniaca era completamente assorbita; la soluzione aveva acquistato una tinta meno carica, e sul fondo del recipiente si era deposta una sostanza non omogenea di un colore giallo nerastro. Questo deposito venne raccolto sopra un filtro, lavato e quindi trattato con acqua bollente, la quale lasciò indisciolti gr. 0,7 di una polvere nera finissima amorfa. La soluzione bollente che aveva un bel color giallo per il raffreddamento depose grammi 1,10 di cloruro di platososemidiammina cristallizzato.

Al liquido poi separato dal miscuglio della sostanza nera e del cloruro di platososemidiammina, aggiunsi un eccesso di cloruro di platosodiammina ed ottenni un abbondante precipitato non omogeneo di colore verdognolo. Questo precipitato trattato alla sua volta con acqua bollente si sciisse in grammi 1,5 del nuovo isomero, che si depose in bei cristalli quadratici per il raffreddamento

(1) Per le ragioni già indicate nel corso di questa memoria al cloruro platinoso, anche in queste esperienze, ho sostituito il cloroplatinito potassico, il quale si può ottenere facilmente e prontamente facendo bollire per pochi istanti fuori del contatto dell'aria una mescolanza in proporzioni convenienti di cloruro potassico e cloruro platinoso insieme a dell'acqua non aerata, senza bisogno di sciogliere prima il cloruro platinoso nell'acido cloridrico come viene indicato nei trattati di chimica.

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The announcement of the conversion of $K[PtCl_3(NH_3)].H_2O$, Cossa's first salt, to the yellow salt $K[PtCl_5(NH_3)].H_2O$, Cossa's second salt, as it appeared in *Gazz. chim. ital.*, 1890, 20, 749

All photographs are by courtesy of Prof. Luigi Cerruti.

Some Platinum Compounds Prepared by Cossa	
Formula	Modern Nomenclature
$2PtpyCl_2$, $Pt(NH_3)_4Cl_2$	$[Pt(NH_3)_4]\ [PtCl_3py]_2$
$2Pt(EtNH_2)Cl_2$, $Pt(NH_3)_4Cl_2$	$[Pt(NH_3)_4]\ [PtCl_3(EtNH_2)]_2$
$2PtNH_3Cl_2$, $Pt(EtNH_2)_4Cl_2$	$[Pt(EtNH_2)_4]\ [PtCl_3NH_3]_2$
$2PtpyCl_2$, $Pt(EtNH_2)_4Cl_2$	$[Pt(EtNH_2)_4][PtCl_3py]_2$
$Cl_2Pt(EtNH_2)_4Cl_2$, $PtCl_2$	$[Pt(EtNH_2)_4]\ [PtCl_6]$
$2Pt(EtNH_2)Cl_2$, $Pt(EtNH_2)_4Cl_2$	$[Pt(EtNH_2)_4]\ [PtCl_3(EtNH_2)]_2$
$2Pt(EtNH_2)Cl_2$, $Ptpy_4Cl_2$	$[Ptpy_4]\ [PtCl_3(EtNH_2)]_2$
$2PtpyCl_2$, $Ptpy_4Cl_2$	$[Ptpy_4]\ [PtCl_3py]_2$
Cl_2, $Ptpy_4Cl_2$, $PtCl_2$	$[Ptpy_4]\ [PtCl_6]$
$PtpyCl_2$, KCl	$K[PtCl_3py]$
$PtpyCl_2$, pyHCl	$pyH[PtCl_3py]$

py = C_5H_5N; $EtNH_2$ = $C_2H_5NH_2$

already prepared monoammine compounds (41, 42). In this work he prepared, among others, the compounds listed in the Table.

The Scottish chemist Thomas Anderson found that when aqueous solutions of $(pyH)_2[PtCl_6]$ and the corresponding compounds of pyridine derivatives are boiled, hydrogen chloride is eliminated with the formation of *cis*-$[PtCl_4py_2]$ (Anderson's platinic compound) or the corresponding compounds of pyridine derivatives, a reaction known as Anderson's reaction (44). Cossa showed that a similar reaction occurs with platinum(II) compounds (43, 45). He first prepared $(pyH)_2[PtCl_4]$ by cooling a mixture of solutions of $K_2[PtCl_4]$ and pyHCl. Boiling an aqueous solution of the compound or heating the solid to 130°C produced *cis*-$[PtCl_2py_2]$.

Cossa also prepared platosomonodiammine compounds, such as platosomonodiammine platinosochloride, $2Pt(NH_3)_3Cl_2,PtCl_2$ (modern $[PtCl(NH_3)_3]_2[PtCl_4]$) (46). In his last article on platinum-ammines Cossa criticised Werner's views of the constitution of both platinum(II)- and platinum(IV)-ammines. He concluded:

> "I put an end to this note by declaring that if I still adhere to Blomstrand's theory, I do not disown the fact that it too does not explain clearly the constitution of the ammoniacal derivatives of platinum; but this theory at least is not in opposition to the majority of the facts ascertained, that characterise this important and numerous series of compounds, that certainly deserves to be illustrated with new and varied experimental researches in order to be able to succeed in finding an even more satisfactory explanation of their structure." (47)

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