

Alfred Werner's Research on the Platinum Metals

A CENTENNIAL RETROSPECT

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Alfred Werner (1866–1919), the founder of co-ordination chemistry, was the first Swiss to receive a Nobel prize in chemistry and is best known for his research on complexes of cobalt. However, he also made many valuable contributions to the chemistry of the platinum group metals, some of which involved resolutions that established the configurations of their complexes.

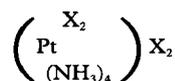
During the 1960s my students and I applied adsorption chromatography to separate a variety of isomeric co-ordination compounds (1–4). Ideally, in order to minimise isomerisation, isomer pairs for separation should be inert, and therefore we began our separations using co-ordination compounds of the platinum group metals. Alfred Werner was also interested in establishing configurations of co-ordination compounds (5, 6) in addition to other stereochemical problems, so he similarly devoted much of his research to complexes of the platinum metals, except palladium.

Platinum

The first of Werner's 14 papers which specifically deals with platinum metal complexes (7–20) is dated 1896 (7). However, he was vitally concerned with the complexes of platinum(II) and (IV) from his first article (1893) on his co-ordination theory, "Beitrag zur Konstitution anorganischer Verbindungen" (21), through a number of theoretical and experimental articles (22–32), books (33, 34), his Nobel Chemistry Prize acceptance address in 1913 (35), and other lectures. For example, in his first article he considered in detail the reactions of *cis*- and *trans*-[PtCl₂(NH₃)₂] (then known as platosemidiammine and platosammine chlorides, respectively) to disprove the Blomstrand-Jørgensen chain theory formulation for these isomers and to argue for a square planar configuration for

platinum(II) and an octahedral configuration for platinum(IV) (21(a), p. 297; 21(b), p. 63). In his first published experimental work in support of his co-ordination theory (22), which he carried out with his friend and former fellow student, Arturo Miolati (1869–1956), he measured the electrical conductances of *cis*- and *trans*-[PtCl₂(NH₃)₂], *cis*- and *trans*-[PtCl₄(NH₃)₂] (then known as platinisemidiammine and platiniammine chlorides, respectively), K[PtCl₃(NH₃)] and K[PtCl₅(NH₃)], Cossa's first and second salt, respectively (36), [Pt(NH₃)₆]Cl₄ (chloride of Drechsel's base), K₂[PtCl₄], and [PtCl₂(NH₃)₄]Cl₂ (Gros's chloride or platinidiammine chloride).

Only the *trans* isomer of the last compound was known then until Chernyaev prepared the *cis* isomer in 1938 (37). However, in a letter to Miolati (38, p. 65) dated May 29, 1897 Werner wrote: "We have also found stereoisomeric platinum compounds of the formula:



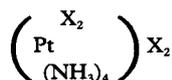
In his first paper on the co-ordination theory Werner had stated, "Until now only one series of these compounds is known", and he was obviously anxious to discover the second series, which would have provided additional support for his theory (21(a), p. 319; 21(b), p. 77). In a letter of May 5, 1898 to an unidentified

The only known photograph of Werner in the laboratory

“Geehrtester Herr Professor”, Werner probably referred again to the same isomers: “As a scientific result I am able to inform you that we have found an octahedral stereoisomerism of platinum, which until now had been observed in cobalt and have thus taken an important step in the experimental foundation of the theory”.



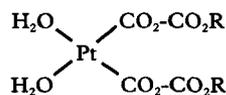
Unfortunately, Werner’s report of his discovery of stereoisomerism among the $[\text{PtX}_2(\text{NH}_3)_4]\text{X}_2$ salts or among any other compounds of platinum(IV) is confirmed only in his letters, not in any of his published articles. In the second paper on conductances, published by Werner and Miolati, are found the two classic V-shaped conductance curves for the transition series (Übergangsreihen) between amines and double salts for both platinum(II) ($[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ to $\text{K}_2[\text{PtCl}_4]$) and platinum(IV) ($[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ to $\text{K}_2[\text{PtCl}_6]$), but there is no mention of isomerism (23(a), 23(b)). Werner may have come the closest to preparing *cis*- $[\text{PtX}_2(\text{NH}_3)_4]\text{X}_2$ in his preparation of the complexes *trans*- $[\text{PtCl}_2\text{pn}_2]\text{Cl}_2$ and *trans*- $[\text{PtBr}_2\text{pn}_2]\text{Cl}_2$ (pn = propylenediamine), both of which occur in only one form (29). When Werner discussed isomerism among platinum(IV) compounds in his book “Lehrbuch der Stereochemie”, he specifically stated that, “Among compounds of the formula



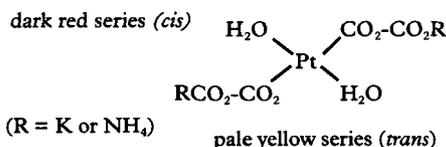
isomerism was until now not observed” (33), and in “Neuere Anschauungen” (34(b), p. 286; 34(c), p. 355; 34(d), p. 366; 34(e), p. 360; 34(f), p. 261) he did not mention the occurrence of isomerism among the salts of $[\text{PtX}_2(\text{NH}_3)_4]\text{X}_2$ (38, p. 68).

The topic of Werner’s first publication devoted specifically to platinum complexes was a series

of researches on the alleged stereoisomerism of platinum compounds, a matter which still remains unsettled (7). Among the hydrated oxalatoplatinates(II) of potassium, ammonium, magnesium, calcium, and cobalt(II), apparently isomeric yellow and reddish copper-coloured salts were known (38, p. 66). In his first article on the co-ordination theory, Werner cited this peculiar isomerism (eigentümliche Isomerie) of these Platinoxalsäuren to support his proposed square planar configuration for platinum(II). He considered the two series to be stereoisomeric, and, on the basis of analogies of colour with platinum(II) complexes of known configurations – an admittedly risky procedure with numerous exceptions – he assigned them as:



and



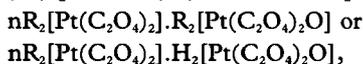
This explanation was disproved by Söderbaum, who found that both series of salts could be dehydrated without change in properties and that the original salts could be re-formed by uptake of water (39, p. 47).

At the time of his first paper on the co-ordination theory, Werner had apparently not



“The Catacombs”, the basement of the Anorganisch-Chemisches Institut, Universität, Zürich, where Werner’s students worked

performed any experimental work on these compounds, but shortly thereafter he assigned the problem to his Swiss Doktorand Friedrich Fassbender (40). In 1896 they published their results (7), but unfortunately no experimental details, such as analyses, were included. In 1899 Werner and his American Doktorand Emil Grebe (41) published a second article on the topic, this time with experimental details (9). Here they reported unstable red salts of a third type, formed by the complete oxidation of the yellow salts and which readily revert to the copper-coloured salts. Such salts were reformulated as platinum(IV) complexes, for example: $R_2[PtCl_2(C_2O_4)_2]$ (7, 9). Werner concluded that the copper-coloured salts were not isomeric with the yellow salts but were instead mixed platinum(III)-platinum(IV) addition compounds:

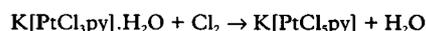


where $R = Na, K, \frac{1}{2}Ca$, (7; 9; 41, p. 10).

As Werner no longer considered the yellow and copper-coloured salts to have the same composition (7), he withdrew his earlier explanation for their stereoisomerism (21(a), p. 317; 21(b), p. 73), noting that “the complete explanation of the ... rather complicated relationships must, however, be relinquished to later investigations” (9, p. 382). Agreement has still not been reached on the relationship between the two series of compounds (38, p. 67). In the discussions of isomerism among platinum(II) com-

pounds in his book published in 1904, Werner cited the Platosoxalsäuren (33, p. 347), but in all the editions of “Neuere Anschauungen” (1905–1923), there is no mention of these compounds (34(a), p. 182; 34(b), p. 286; 34(c), p. 357; 34(d), p. 367; 34(e), p. 362; 34(f), p. 261).

In his paper published in 1896 Werner also prepared potassium trichloropyridineplatinatate(II), analogous to Cossa’s first salt ($K[PtCl_3(NH_3)] \cdot H_2O$) (35), and he oxidised it to potassium pentachloropyridineplatinatate(IV), analogous to Cossa’s second salt ($K[PtCl_5(NH_3)] \cdot H_2O$) (36):



In 1897 he and Fassbender prepared the rubidium and caesium salts of the platinum(II) series and the lithium, sodium, rubidium, caesium, and pyridinium salts of the platinum(IV) series (8). In a study of ethylenediamine and propylenediamine complexes Werner also prepared $[Pt(en)_2]Cl_2$, $[Pt(pn)_2]X_2$ ($X = Br, I$), $[Pt(NH_3)_2(pn)]Cl_2$, *cis*- $[PtCl_2, pn]$, $[PtX_2, pn_2]Cl_2$ ($X = Cl, Br$), $[PtCl_2, pn]$, and $[PtBr_2(NH_3)_2, pn]Cl_2$ (29, pp. 121–127).

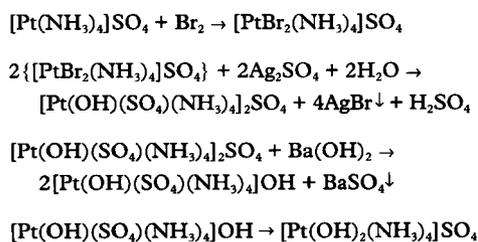
Of the metal- β -diketone chelates, the acetylacetonate compounds have found extensive analytical applications in gas chromatography because of their volatility. In the apt words of Morgan and Moss, these ligands gave “wings to the metals” (42). In 1901 Werner prepared acetylacetonate derivatives of platinum(II) (10), which, like the oxalato complexes discussed

above, are very stable chelate compounds with the platinum atom linked to two oxygen atoms in each ring. In the presence of alkali, acetylacetone reacted with $K_2[PtCl_4]$ to form four different products:

- (i) $K[PtCl_2A]$ (A = acetylacetonate ion), tetravalent monochelate
- (ii) $M[PtCl_2A_2]$ (M = Na, K, Rb, H), dichelate, apparently 5-covalent; the acid exists in two forms; according to Werner, one contains the keto form and the other contains the enol form
- (iii) $Na_2[PtCl_2A_2]$, dichelate, 6-covalent
- (iv) $[PtA_2]$, dichelate, tetravalent.

Also in 1901, Werner and his American post-doctoral co-worker Charles Holmes Herty (1867–1938), who later became president of the American Chemical Society (1915–1916), prepared and measured the conductances of a number of non-electrolytic platinum(II) and platinum(IV) complexes: *cis*- and *trans*- $[PtCl_2(NH_3)_2]$, *cis*- and *trans*- $[PtCl_4(NH_3)_2]$, and *cis*- $[PtCl_2A]$ (A = ethylenediamine or propylenediamine) (30).

In 1907, as Part V of his series “Zur Theorie der Hydrolyse” (14), Werner examined the properties and reactions of the tetraamminedihydroxoplatinum(IV) salts, first synthesised by Carlgren (43). Werner prepared the sulfate, which exists both as a tetrahydrate as well as an anhydrous salt, by the following reactions:



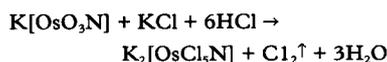
Werner also prepared the corresponding chloride and bromide and by using conductance measurements showed that the hydroxo groups do not ionise, but are firmly bonded to the platinum atom. They also fail to be converted to co-ordinated water on treating the salts with acid.

By 1917 Werner, who was now suffering from the illness that was to prove fatal, had already proven the octahedral configuration for

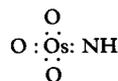
complexes of cobalt(III), chromium(III), iron(II), rhodium(III), and iridium(III) by the resolution into optical isomers of their tris-bidentate and other types of complexes. In the first article of a projected but never continued series, “Über Spiegelbildisomerie bei Platinverbindungen”, he was the first to describe the preparation of the tris(ethylenediamine)platinum(IV) salts, $[Pt(en)_3]X_4$ (18, 44). He resolved the chloride, iodide, thiocyanate, and nitrate by means of ammonium (+)- and (-)-tartrate, which simultaneously showed that optical isomerism could exist among co-ordination compounds of tetrapositive elements and confirmed the octahedral configuration that he had proposed in 1893 for Pt(IV) in his first article on the co-ordination theory (21(a), p. 297; 21(b), p. 47). This configuration has since been amply corroborated by numerous resolutions, including those of the trisbidentate chelates of platinum(IV) with (+)- and (-)-propylenediamine, carried out by his assistant A. P. Smirnoff and published after Werner’s death (45).

Osmium

Osmium, like rhenium, which adjoins it in the Periodic Table, forms a variety of nitrido complexes, especially in the VI oxidation state (46, 47). Osmium halonitrido complexes occur in two series, both of which were discovered by Werner and Karl Dinklage, his Doktorand from Bohemia (48). They prepared red potassium nitrilopentachloroosmiumate (modern, pentachloronitridoosmate(VI)) (octahedral) by treating potassium osmiumate (modern, nitrodoosmate(VIII)) with hydrochloric acid and potassium chloride (11; 48, p. 206):



They also prepared the corresponding ammonium, rubidium, and caesium salts by metathesis and proposed



as the constitution of osmiumic acid (now known

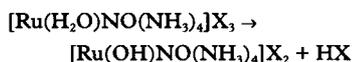
to be tetrahedral). In a second article they prepared the ammonium, rubidium, and caesium hydrogen salts of the corresponding bromo complex, $[\text{OsBr}_2\text{N}]^{2-}$, as well as the potassium salt – the only known salt of the second series of halonitrido complexes – the dark red $\text{K}[\text{OsCl}_4\text{N}]$ (12), which has been shown to have a square pyramidal configuration (50).

Ruthenium

Werner wrote two articles on ruthenium complexes, the first appearing in 1907 as Part III of his series “Zur Theorie der Hydrolyse” (13). In order to investigate the behaviour of the hydroxo group bonded to a metal atom, Werner prepared and characterised four series of *trans*-tetraamminenitrosylruthenium(III) complexes, some of which had been previously prepared by Claus (51) and formulated by Joly (52):

- (a) $[\text{Ru}(\text{OH})\text{NO}(\text{NH}_3)_4]\text{X}_2$ (X = Br, I, NO_2 , Cl)
- (b) $[\text{Ru}(\text{H}_2\text{O})\text{NO}(\text{NH}_3)_4]\text{X}_3$ (X = Br, NO_2 , Cl, $\frac{1}{2}\text{SO}_4$)
- (c) $[\text{RuCl}(\text{NO})(\text{NH}_3)_4]\text{X}_2$ (X = Cl, $\frac{1}{2}\text{PtCl}_4$, I, NO_2)
- (d) $[\text{RuBr}(\text{NO})(\text{NH}_3)_4]\text{X}_2$ (X = Br, I, NO_2 , $\frac{1}{2}\text{SO}_4$).

The hydroxo complex (a) was prepared by treating $\text{M}_2[\text{RuCl}_5(\text{NO})]$ with ammonia. The aqua complexes (b) are very unstable and on dissolving in water form the hydroxo complexes (a):



In his second article on ruthenium, his penultimately published article, Werner and A. P. Smirnoff prepared the corresponding hydroxynitrosylbis(ethylenediamine)ruthenium(III) compounds, $[\text{Ru}(\text{OH})\text{NO}(\text{en})_2]\text{X}_2$ (corresponding aqua complexes do not exist) (20). Several modern reviews have been devoted to transition metal nitrosyl complexes (53–55).

Iridium

The first of Werner’s two articles on iridium complexes (15) was co-authored with his assistant Otto de Vries (56), son of the Dutch botanist Hugo Marie de Vries, who proposed the mutation theory. They prepared and characterised a number of iridium(III) complexes,

which they found to be analogous to the corresponding cobalt(III) complexes, but much more stable. The compounds included:

$\text{M}_3[\text{IrCl}_2(\text{NO}_2)_4]$ (M = Na, K); $[\text{Ir}(\text{NO}_2)_5(\text{NH}_3)_3]$; $[\text{Ir}(\text{NO}_2)_2(\text{NH}_3)_4]\text{X}$ (X = Cl, Br, $\frac{1}{2}\text{SO}_4$, NO_2); $[\text{IrNO}_2(\text{NH}_3)_5]\text{X}$ (X = Cl, I, $\frac{1}{2}\text{SO}_4$); $[\{\text{IrNO}_2(\text{NH}_3)_5\}\text{SO}_4] \cdot 3\text{H}_2\text{SO}_4$; $[\text{IrNO}_2(\text{NH}_3)_5](\text{NO}_2)_2$ and $[\text{IrCl}_2(\text{NH}_3)_4]\text{X}$ (X = Cl, Br, I, $\frac{1}{2}\text{SO}_4$, $\frac{1}{2}\text{IrCl}_6$).

In his second article on iridium (20), published posthumously with his assistant A. P. Smirnoff, Werner prepared and resolved into enantiomers two series of iridium(III) complexes: *cis*- $[\text{Ir}(\text{NO}_2)_2\text{en}_2]\text{X}$ and $[\text{Iren}_3]\text{X}_3$, using silver α -(+)- and (-)-camphorsulfonate and sodium α -(+)-nitrocamphorate, respectively, as resolving agents (44, p. 137). The *cis*- $[\text{Ir}(\text{NO}_2)_2\text{en}_2]\text{X}$ compounds closely resemble the *cis*- $[\text{Ir}(\text{NO}_2)_2(\text{NH}_3)_4]\text{X}$ salts first prepared by Werner and de Vries (13). As no *trans* compounds were isolated, the resolutions simultaneously proved the *cis* configuration and with the resolution of $[\text{Iren}_3]\text{X}_3$, confirmed the octahedral configuration for iridium that had been proposed in 1914 by Delépine (57). Delépine and Charonnat’s “active racemate” method (58) and Mathieu’s rotatory dispersion studies (59) confirmed Werner’s solubility rule (16, 60, 61) and showed that the (-)- $[\text{Iren}_3]^{3+}$ ion possesses the same configuration as the (+)- $[\text{Coen}_3]^{3+}$, (+)- $[\text{Cren}_3]^{3+}$, and (-)- $[\text{Rhen}_3]^{3+}$ ions.

Rhodium

The two papers that Werner published on rhodium complexes were part of his programme to determine the influence of the nature of the central metal atom on optical rotatory power (32). In 1912 Werner was the first to prepare the extremely stable tris(ethylenediamine)-rhodium(III) salts, specifically for the purpose of attempting their resolution (16; 44, p. 135; 62). In the first of his two articles titled “Über Spiegelbild-Isomerie bei Rhodium-Verbindungen” (16), he not only established the existence of optical isomerism and the octahedral configuration for another metal – the first configuration for a platinum metal – but he also enunciated a valuable empirical rule for determining

the generic configuration of optically active complexes, the previously mentioned principle which became known as Werner's solubility rule that he later developed and extended (60). Together with the rotatory dispersion technique developed by Mathieu (59), it is probably the most important method for determining the relative configuration of complexes.

Werner had realised that the absolute configuration of a complex cannot be determined directly from the sign of optical rotation (60, 63). According to his solubility rule, all antipodes of a corresponding type which give the least soluble diastereoisomer with a given resolving agent have the same absolute configuration, regardless of the sign of rotation. Applying this rule to the resolution of the $[\text{Men}_3]^{3+}$ complexes of cobalt(III), chromium(III), and rhodium(III) by means of (+)-nitrocamphorates and (+)-tartrates, Werner concluded that the (+)-[Coen₃]³⁺, (+)-[Cren₃]³⁺, and (-)-[Rhen₃]³⁺ cations possess the same absolute configuration.

The stable, water-soluble trioxalatorhodates(III) were discovered by Leidié in 1899 (64). In his second rhodium article, in 1914 (17), Werner and J. Poupardin, resolved the potassium salt of trioxalatorhodates(III) with strychninium nitrate and then isolated the sodium, rubidium, and barium salts. They found that the rhodium salts do not racemise appreciably, even in hot solution, and are much more stable than the corresponding chromium compounds (44, p. 136). Also, by cooling a hot, concentrated solution of the racemic mixture, they claimed to obtain hemihedral crystals of (+)- and (-)-K₃[Rh(C₂O₄)₃], which they separated mechanically with the aid of a microscope. This would have been the first successful application of Pasteur's method of spontaneous resolution by conglomerate crystallisation to co-ordination compounds. Jaeger was unable to duplicate their results with this compound (65), but he and Thomas were able to resolve K₃[Co(C₂O₄)₃] into its optical antipodes in a similar manner (66, 67). Some questions have arisen about the number of molecules of water of crystallisation contained in optically active K₃[Rh(C₂O₄)₃], and Bernal and Kauffman have recently



Alfred Werner (right) and fellow student Arturo Miolati outside the Eidgenössisches Polytechnikum, in January or February, 1893. Fellow students Franz Feist and Roland Scholl are peeping from the door

questioned discrepancies in some of Werner and Poupardin's results (68). In the dissertation of Wera Tupizina, one of Werner's numerous Russian Doktorandinnen, the resolution of $[\text{Rh}(\text{C}_2\text{O}_4)_3\text{en}_2]\text{X}$ ($[\alpha] = +153^\circ$ to $+275^\circ$) is mentioned, but the work was never published (69).

Alfred Werner not only made a number of valuable contributions to the chemistry of the platinum metals, but he also used these results to introduce the concept of optical activity, so widespread in organic chemistry, into inorganic chemistry.

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