

# **THE CHEMISTRY OF PLATINUM AND PALLADIUM**

**With Particular Reference to  
Complexes of the Elements**

**F. R. HARTLEY**

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**F. R. HARTLEY**

**M.A., D.Phil., A.R.I.C.**

*University of Southampton, Great Britain*



**APPLIED SCIENCE PUBLISHERS LTD  
LONDON**

**APPLIED SCIENCE PUBLISHERS LTD  
RIPPLE ROAD, BARKING, ESSEX, ENGLAND**

**ISBN: 0 85334 543 0**

**WITH 59 ILLUSTRATIONS AND 129 TABLES**

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**Printed in Great Britain by J. W. Arrowsmith Ltd., Bristol, England.**

## Preface

This monograph has been written for three reasons: they are first, the author's general interest in these two metals and his special interest in certain aspects of their chemistry; secondly, the large output of original research from many centres since the Second World War; and thirdly, the absence of a recent survey covering the literature dealing with platinum and palladium. Within the limits of the space available, the present text constitutes a reasonably comprehensive account of the subject matter. It more than adequately meets the probable needs of students and teachers and, because of the extensive documentation, should provide a convenient place of first reference for those already involved in research. To those embarking upon such work, the author hopes it offers both suggestion and guidance. All concerned with laboratory investigation should find the two appendices of special service: one gives essential details of the preparation and properties of the compounds of platinum and palladium usually employed as starting materials for further experimentation; the other sets out a complete, up-to-date list of the published structures of the compounds of these elements arranged so as to serve as an immediate source of data for correlation purposes.

Platinum and palladium have attracted continuing attention largely because they have been the source of an increasing stream of new compounds of high intrinsic interest, particularly with respect to bonding and structure. The kinetics of the reactions involved in their formation and utilisation have been the object of much enquiry. Their organometallic chemistry is extensive; and they have excited interest as homogeneous and heterogeneous catalysts; and the breakthrough to the fixation of some of the noble gases initiated by the preparation of xenon hexafluoroplatinate(V) has led to notable results. In the monograph emphasis has been laid on structure and bonding, and an attempt has been made to evaluate critically the role of the physical techniques currently used to elucidate these problems. Attention has been called to the need to appreciate the scope and limitations of present theories of bonding as they are applicable to the complexes of these elements.

A brief run-down of the contents of the monograph may help the reader by showing how the subject-matter has been subdivided and grouped. Beyond the introductory chapter the oxidation states are summarised and their class 'b' or 'soft' character is discussed. Then follow through several chapters an extended consideration of zerovalent, divalent and tetravalent

states. The treatment is comparative and designed to display similarities and differences between the respective chemistries of platinum and palladium; as a help to this end much use has been made of tables. Throughout, the diagnostic techniques employed have been stressed and structure and bonding given a prominent place. From this the monograph passes on to deal with substitution reactions, associative mechanism in reactions of square-planar complexes, and isomerism in compounds of the elements in a divalent state. Then follow accounts of metal-carbon  $\sigma$ -bonded compounds, olefin and acetylene complexes, and finally the  $\pi$ -allyl complexes which are of interest both for their bonding and their significance in reactions catalysed by palladium(II) salts.

I am indebted to Professor L. M. Venanzi for first introducing me to inorganic chemistry in general and the chemistry of these two metals in particular, and to the late Professor Sir Ronald Nyholm FRS for later fostering this interest. I should like to thank Professor P. L. Robinson for critically reading the drafts of each chapter and for the many helpful suggestions which he made for their improvement. Finally I should like to thank my wife both for her patience during the writing of this book and for her help in handling the large amount of information which had to be sifted before this book could be written.

F. R. HARTLEY  
Southampton

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## CHAPTER 1

### Introduction

This chapter is in two parts. The first provides an introductory survey of the scope of the monograph which, as the sub-title indicates, and as the character of the chemistry of platinum and palladium demands, is mainly about the complexes of these elements. The second part gives brief notes on the occurrence, extraction and properties of the elements and their uses, especially that of the metals as such.

#### INTRODUCTORY SURVEY

A systematic study of the chemistry of platinum began soon after its arrival in Europe in 1741 and by 1830 not only had many of the inorganic compounds been made but the first organometallic derivative  $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]\cdot\text{H}_2\text{O}$  had actually been prepared.<sup>(1)</sup> Palladium was discovered in 1803, and the chemistry of both metals developed during the rest of the nineteenth century and, with increasing acceleration, in the twentieth century, in the course of which the empirical facts and the theoretical significance of covalence were recognised. There were three factors which attracted interest to and sustained research on these two metals.

First, in the divalent oxidation state both readily form complexes with ligands containing donor atoms from most groups of the periodic table. Following from this the nineteenth and early twentieth centuries saw the preparation of many crystalline platinum derivatives as a routine method of characterising organic compounds; from this much information on the co-ordination chemistry of platinum flowed.

Secondly, there came the recognition of the square-planar geometry of the divalent oxidation states, which opened up the possibility of *cis-trans*-isomerisation in such complexes. From this followed the discovery of the *trans*-effect in platinum(II) complexes in the 1920's (pp. 299-301).<sup>(2)</sup> Its elucidation enabled the systematic synthesis of any desired platinum(II) complex to be accomplished. These extensive researches reached their peak with the synthesis of all the three possible geometric isomers of  $[\text{Pt}(\text{pyr})(\text{NH}_3)\text{BrCl}]$ .<sup>(3)</sup> From 1930 to 1950 was a period of consolidation in which a great deal of the coordination chemistry of the two metals was systematised.

Thirdly, on the basis of this not inconsiderable achievement, but much stimulated by advancing theory, there followed a tremendous growth in

interest in platinum and palladium triggered off by the burgeoning of their organometallic chemistry. This is a vast subject of great intrinsic interest. It has applications in the field of homogeneous catalysis in the reactions of organic compounds, and also provides some basis for a discussion of the mechanisms of organic reactions that are heterogeneously catalysed by the metals themselves and by their oxides.

The commonest oxidation state for both metals is +2. There are also many compounds with the elements in the zero and +4 oxidation states, although these are both much commoner for platinum than palladium. For instance on heating in chlorine, platinum forms a mixture of  $\text{PtCl}_2$ ,  $\text{PtCl}_3$  and  $\text{PtCl}_4$ <sup>(4,5)</sup> whereas palladium forms only the dichloride  $\text{PdCl}_2$ .<sup>(6)</sup> In the +4 oxidation state both metals exhibit octahedral coordination. The greater reluctance of palladium to form +4 compounds, owing to the higher ionisation energy needed to produce  $\text{Pd}^{4+}$  than  $\text{Pt}^{4+}$  ions (p. 13) has two important consequences: the first and most apparent (p. 251) is that there is a much wider range of platinum(IV) than palladium(IV) compounds; the second, and less obvious consequence, is that whereas many complexes of platinum(II) undergo reactions by an oxidative-addition mechanism (pp. 329-31 and pp. 339-340) such a mechanism is generally not available to palladium(II) complexes. Either the palladium(II) complexes do not react or the vigorous conditions are required to promote reaction by an alternative, higher energy, path.

In their zerovalent oxidation states both metals form a range of complexes (pp. 27-47). Although these might possibly be prepared by treating the metal with the ligand, in practice they are usually obtained from the divalent compounds with the aid of a suitable reducing agent.

Although compounds of the metals in the zero, +2 and +4 oxidation states are common, compounds in the +1 oxidation-state (pp. 16-17) are very difficult to make. Compounds in the +3 state have not been unambiguously identified for either metal. Moreover, platinum alone forms a fluoride and oxyfluoride in the +5 state as well as the hexafluoride  $\text{PtF}_6$ , in the +6 oxidation state. Reasons for each of the metals forming compounds in a particular oxidation state are examined in Chapter 2 and in the same place a general survey of all the oxidation states is given. It is also shown that in oxidation states below +4 the two metals are class 'b' or 'soft' acids (pp. 13-15).

In Chapters 4 to 9 compounds and complexes of the elements in the divalent condition are considered, the donor atoms bound directly to the metal are classified according to their positions in the periodic table. Chapter 10, dealing with compounds and complexes of the metals in the tetravalent state, brings out the important point that there is sufficient similarity between the square-planar platinum(II) and octahedral platinum(IV) complexes to enable many of the properties of platinum(IV) complexes to be understood by looking upon them as square-planar platinum(II) complexes with two extra ligands bound one above and one below the plane.

Some topics could not be conveniently covered within the scope of Chapters 4 to 9. Of these the most important is the mechanism of the reac-

tions, particularly the substitution reactions, of the two elements; this subject is enlarged upon in Chapter 11. Most of the information available relates to platinum complexes, because these react much more slowly than their palladium counterparts and are generally amenable to the simple experimental techniques devised to follow slow reactions. On the other hand palladium complexes, with certain exceptions, call for the use of more expensive equipment designed to measure the rates of fast reactions. However, conclusions involving platinum complexes have generally been assumed to apply to corresponding reactions of palladium complexes. When tested experimentally these assumptions have generally been found to be valid.

A current major growth area in the study of platinum and palladium has been that of their organometallic chemistry. Some dramatic results in the homogeneous catalysis of the reactions of organic compounds, particularly the successful commercial exploitation of the Wacker one-stage process for the homogeneous catalytic oxidation of ethylene to acetaldehyde in the presence of palladium(II) chloride (pp. 388-389), have contributed to this interest. The organometallic chemistry might have been included in the earlier chapters; this was not done because in this instance the oxidation state of the metal is of less importance than the nature of the ligand. Accordingly, the final three chapters deal, respectively, with metal-carbon  $\sigma$ -bonded compounds, olefin and acetylene compounds, and  $\pi$ -allylic compounds. In these chapters structure and bonding has been especially emphasised because this knowledge is essential to an understanding of the chemistry of the organometallic compounds. A feature which emerges in Chapters 12 to 14 is the complementary nature of the properties of platinum and palladium in organometallic compounds. Thus platinum forms more stable compounds with alkyl and olefinic ligands than palladium, but the reverse is true of their behaviour with  $\pi$ -allylic ligands. Although this cannot as yet be fully explained, some tentative suggestions towards this end are advanced in Chapter 14 (p. 441).

## RESUMÉ OF THE OCCURRENCE, EXTRACTION AND PROPERTIES OF PLATINUM AND PALLADIUM

Platinum, discovered in the sixteenth century in the Choco district of Columbia, was originally called '*platina del Pinto*' or 'little silver of the Pinto River'.<sup>(7)</sup> Charles Wood, an Assay Master of Jamaica, brought it to Europe in 1741 and passed the specimen by way of William Brownrigg FRS to Sir William Watson FRS who described it to the Royal Society in 1750.<sup>(8)</sup> A fairly definitive account of platinum was published in 1755 and 1757 by William Lewis FRS, a medical practitioner of Kingston-upon-Thames.<sup>(9)</sup>

Palladium was discovered in 1803, some three hundred years after platinum, by W. H. Wollaston FRS when he was investigating the refining of platinum and it was named after the recently discovered asteroid Pallas.<sup>(10)</sup>

### Occurrence

Platinum occurs as metal, and before 1914 most of it came from Russia and Columbia; today the sources of native platinum are Alaska and Columbia,

but their contribution represents only a very minor part of world production. Nearly all platinum is derived from the copper-nickel ores of Canada, South Africa and Russia, and they contain less than an ounce of platinum per ton.

Palladium occurs in association with platinum; the Canadian ores have more palladium than platinum, whereas the reverse is true of the South African ores. Incidentally, the native platinum found in Columbia contains between 0.5 and 3% of palladium.

### Extraction

The platinum and palladium in cupronickel ores are recovered along with other noble metals from the anode slimes produced in the electrolytic recovery of the copper and nickel or from the involatile residues from the Mond carbonyl process for refining nickel. Figure 1 outlines the treatment of the concentrates.<sup>(11)</sup> This begins with aqua-regia which is used to dissolve the platinum, palladium and gold. Because platinum is more easily oxidised

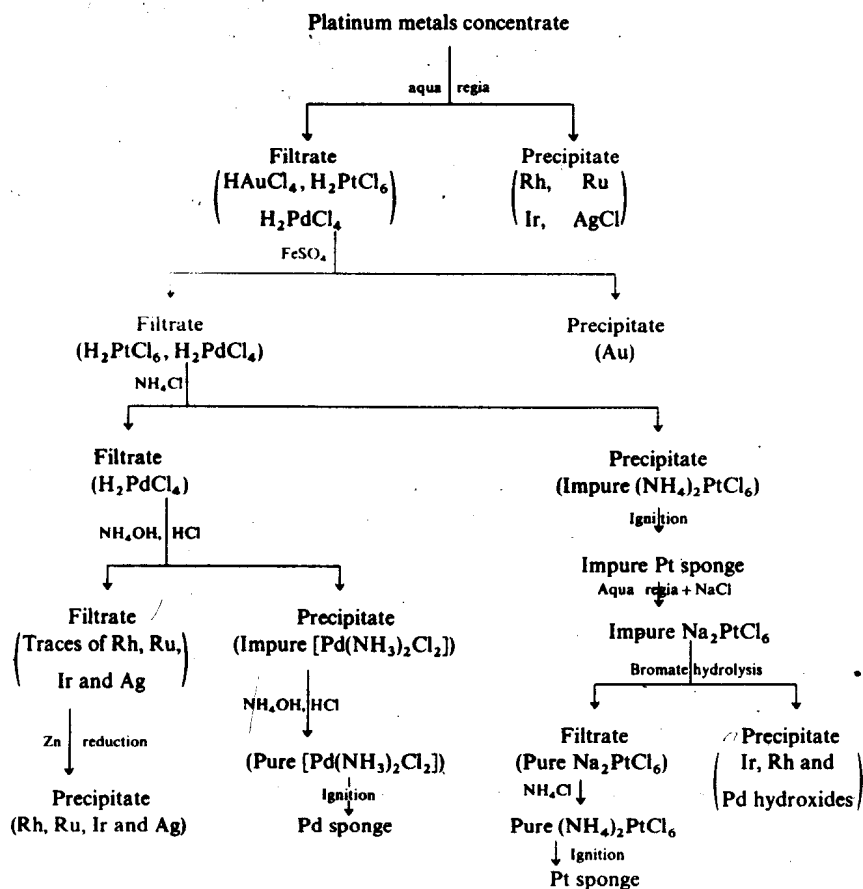
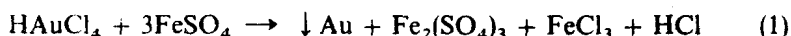


Fig. 1. Scheme for the extraction of platinum and palladium.

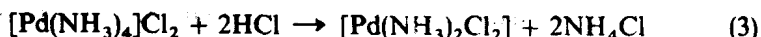
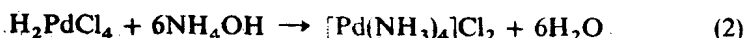


than palladium (p. 13) the former reaches the +4 and the latter only the +2 oxidation state. This solution is treated with either ferrous sulphate or chloride which reduces chloroauric acid to gold, leaving platinum and palladium in solution (eq. 1). The addition of ammonium chloride precipitates orange-



yellow ammonium hexachloroplatinate(IV), which is filtered off and ignited to give an impure platinum sponge. This crude sponge is dissolved in aqua-regia, filtered and evaporated with sodium chloride and hydrochloric acid to remove nitric acid and nitrosyl compounds and convert the platinum to water-soluble sodium hexachloroplatinate(IV). The sodium hexachloroplatinate(IV) solution is then treated with sodium bromate to oxidise the remaining impurities (Ir, Rh and Pd) to valence states from which, by a careful addition of sodium bicarbonate the metals are quantitatively precipitated as dark slimy hydroxides. The pure filtrate is then boiled with hydrochloric acid to destroy the excess of bromate and treated with ammonium chloride to precipitate platinum as ammonium hexachloroplatinate(IV); this is filtered off, washed, dried and finally heated very slowly up to 1000°C to give >99.9% pure platinum sponge.

The impure palladium salt ( $\text{H}_2\text{PdCl}_4$ ) is treated with dilute ammonia (eq. 2) and precipitated as  $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$  by hydrochloric acid (eq. 3). The process is repeated to yield pure  $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$ , which is filtered off and



ignited to palladium sponge. To avoid the formation of an oxide film the sponge is cooled in hydrogen. The product is >99.9% palladium.

### Physical and chemical properties

Platinum and palladium are grey-white, lustrous metals which are sufficiently ductile and malleable to be drawn into wire, rolled into sheet or formed by spinning and stamping. They have high melting-points and considerable resistance to corrosion. Their main physical properties are summarised in Table 1 which gives the currently acceptable values, some of which are critically dependent on purity.

Both platinum and palladium are noble metals owing to a combination of high sublimation energy and high ionisation potential (p. 9). Of the two metals, platinum is slightly the less reactive. It is not attacked by any single mineral acid but readily dissolves in aqua-regia, whereas palladium, even in the compact state, is attacked by hot concentrated nitric and sulphuric acids, particularly in the presence of oxygen and the oxides of nitrogen. In powder form palladium is slowly dissolved by hydrochloric acid in the presence of oxygen. Platinum is not oxidised when heated in air whereas palladium is oxidised to palladium(II) oxide in air at 700°C. Above 875°C the oxide dissociates to the free metal and oxygen.<sup>(15)</sup> Palladium, but not platinum, is attacked by moist chlorine and bromine at room temperature.