

IPA

**PHYSICAL AND
CHEMICAL
PROPERTIES
OF PLATINUM
GROUP METALS**



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SUMMARY

- Six elements of Groups 8, 9, and 10 in the periodic table constitute the platinum group metals (PGMs): platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir), and osmium (Os).
- The physical and mechanical properties of the PGMs and their compounds indicate a wide range of properties with widely varying densities and solubilities (see Table 2-1).
- Metallic forms of PGMs are generally considered to be 'inert', *i.e.*, not chemically reactive. However, this is dependent in part on dimensional characteristics. Thus, while massive metal forms have low chemical reactivity, finely-divided metal powders with high surface area show greater reactivity.
- Simple binary compounds exist for each of the PGMs. They also form a vast array of complex coordination compounds in which the central metal atom is bound to a variety of ligands by coordinate bonding, including halides, sulphur, amines, and other atoms and groups.
- This unique coordination chemistry has made PGM compounds of great industrial value, but also can have implications for the health of workers exposed to certain of these compounds due to the linkages with biological behaviour and toxicity (see Chapter 6).
- The complex halogenated platinum compounds (CHPS) are among those which are industrially and toxicologically important.
- Other commercially significant forms of PGMs include, but are not limited to: metallic PGMs; ammine complexes of platinum and palladium; chloro-compounds other than those in the CHPS series; rhodium salts; and the PGM nitrates.

2.1

OVERVIEW OF PGMs

The six platinum group metals (PGMs) are transition metals occurring in the d-block (groups 8, 9, 10, periods 5 and 6) of the periodic table (Figure 2-1).

These metals, along with silver and gold, share a generally high resistance to chemical attack and, as a result, are also called the

'noble metals'. In common with the other transition elements, their chemistry is characterised by multiple oxidation states and a wide range of coloured compounds covering the entire spectrum from, commonly, almost colourless (osmium), through yellows (platinum) to rich red-browns (palladium, iridium,

ruthenium), reds (rhodium) and, less commonly, purples and blues (ruthenium and iridium). They form a vast range of coordination compounds with some of the most complicated and diverse chemistry in the periodic table.

Manganese 25 Mn	Iron 26 Fe	Cobalt 27 Co	Nickel 28 Ni	Copper 29 Cu
Technetium 43 Tc	Ruthenium 44 Ru	Rhodium 45 Rh	Palladium 46 Pd	Silver 47 Ag
Rhenium 75 Re	Osmium 76 Os	Iridium 77 Ir	Platinum 78 Pt	Gold 79 Au
Bohrium 107 Bh	Hassium 108 Hs	Meitnerium 109 Mt	Darmstadtium 110 Ds	Roentgenium 111 Rg

Figure 2-1: Platinum Group Metals in the Periodic Table

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METALLIC PGMs

Metallic forms of PGMs are generally considered to be 'inert', but this is dependent in part on dimensional characteristics.

Reactions of PGMs with most substances, for example oxygen, halogens, and acids, are influenced—both in rate and extent—by the particle size of the metal. Thus some reactions that apparently do not take place with massive metal can occur with finely-divided, high surface area metal powders. The metals in colloidal form (as 'blacks') can exhibit striking catalytic capabilities in some reactions.

PGMs are all susceptible to attack by elemental halogens, especially chlorine and fluorine. Palladium, platinum, and to a lesser extent, rhodium are attacked to varying

degrees by mineral acids such as nitric, sulphuric or aqua regia (a mixture of hydrochloric and nitric acids), particularly when finely divided. On a laboratory scale iridium, ruthenium, and osmium (sometimes called the 'insoluble PGMs'), usually require fusion with an oxidising alkali, such as sodium peroxide, followed by acidification with hydrochloric acid to reliably solubilise them, particularly after high-temperature treatment.

Metallic PGMs provide perhaps the most commercially important class of catalysts known and include automotive exhaust catalysts, petroleum platforming catalysts, ammonia oxidation catalysts, and fuel cells. See Chapter 3 for further information regarding applications of PGMs.

2.3

COMPOUNDS OF PLATINUM GROUP METALS

COMPOUNDS OF PLATINUM GROUP METALS

For more comprehensive reference sources on the characteristics, chemistry, and physic-chemical properties of PGMs and their compounds the reader is referred to various reference sources (O'Neil, 2001; Sehrt and Grehl, 2012). Supplier Company catalogues and websites also contain useful information on these aspects including those of Johnson Matthey, Umicore N.V., Heraeus GmbH and BASF. The biological properties and toxicology of PGMs are separately addressed in Chapter 6 of this Guide.

PGMs form a number of apparently simple binary compounds which are invariably structurally complicated. They also form a vast array of coordination compounds in which the central metal atom is bound to a number of ligands by coordinate bonding, including halides, sulphur, amines, and other atoms/groups. This unique coordination chemistry has made PGM compounds of great industrial value, but also can have implications for the health of workers exposed to certain of these compounds due to linkages with biological behaviour and toxicity (see Chapter 6).

SIMPLE COMPOUNDS

In the environment, platinum group metals occur separately, or alloyed together, or alloyed with other metals (e.g., as osmiridium and ferroplatinum). There are also some distinct compound mineral species which illustrate the binary compounds: these include sperrylite (PtAs_2); cooperite (Pt,PdS); a series of platinum and palladium chalcocides, such as sulfarsenides, michenerite (PdBiTe) and moncheite (Pt,Pd(Te,Bi)_2); and laurite, (Ru,OsS_2); all of which occur naturally in metal sulphide deposits, such as in Sudbury, Ontario in Canada and in the Merensky Reef in South Africa.

Binary compounds exist for each metal. The most important compounds are those with oxygen or chlorine. Platinum(IV) oxide is a commercially used catalyst. Iridium, rhodium, and palladium(IV) hydrated oxides can be used to quantitatively hydrolyse these metals during refining, and the volatile

ruthenium(VIII) and osmium(VIII) oxides are frequently used to recover these metals by distillation. Although PGMs form binary anhydrous chlorides, these are not commercially significant. They are often substantially insoluble in most solvents, and polymeric in structure.

2.3

COMPOUNDS OF PLATINUM GROUP METALS

COMPLEX COMPOUNDS

In common with all transition metals, the vast majority of the commercial chemistry of PGMs is concerned with their extensive range of coordination complexes. In these, the central metal atom is bound to a number of ligands, or complexing agents. These ligands are atoms or molecules which frequently act as electron donors. The biological significance of ligand substitution is discussed in more detail in Chapter 6.

As a generalisation, in the early 1960s Pearson developed a set of 'rules' for 'hard/soft' Lewis acids (Pearson, 1963). The platinum group metals are categorised as 'soft' metals that prefer to coordinate to 'soft' ligands (e.g., cyanide, ammonia, amines, sulphur ligands and halides, etc.). They do not easily form complexes with 'hard' ligands, such as oxo acids (e.g., nitrate, sulphur, phosphate, etc.). The practical use of complex compounds of PGMs in homogeneous and heterogeneous catalysis has generated further rapid development of their chemistry. This is discussed below, and also in Chapter 6 with specific reference to how the chemistry of these compounds relates to their toxicity.

Chloride solutions are the predominant media for the commercial separation and refining of PGMs. In this application, PGMs form sequences of aquated species with the relatively weakly bound chlorides such as the hexagonal $[M(\text{Cl})_n(\text{H}_2\text{O})_{6-n}]^{4-n}$, where M is Pt(IV) or Ir(IV), or the square planar $[M_1(\text{Cl})_n(\text{H}_2\text{O})^{4-n}]^{(2-n)}$, where M_1 is Pt(II) or Pd(II). The degree of aquation increases with decreasing chloride concentration. The ammonium and potassium salts of some of the hexachloro complexes are of relatively low water solubility and those of Pt(IV), Pd(IV), and Ir(IV) are sometimes used for precipitation of those metals during refining and purification processes.

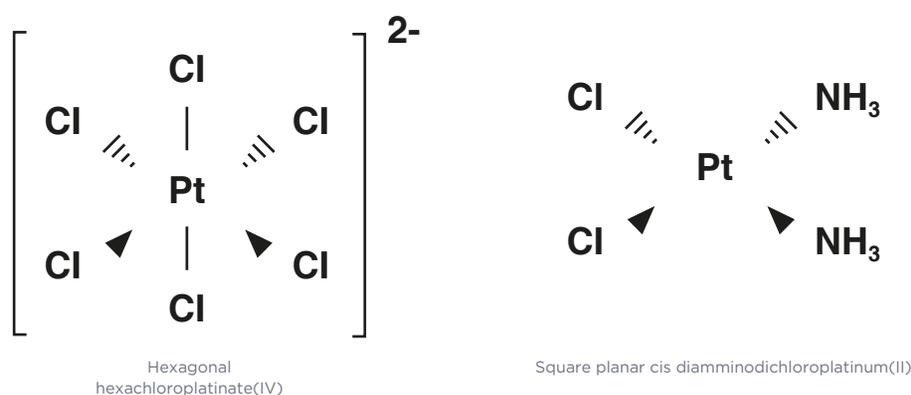


Figure 2-2: Example structures of Pt coordination complexes

2.3

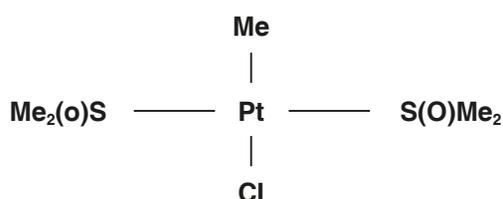
COMPOUNDS OF PLATINUM GROUP METALS

Another commercially important class of compounds are the amine and ammine complexes of platinum(II), palladium(II) and platinum(IV). The ammine complexes of the latter find application in electroplating and automotive exhaust catalyst production. Diamminedichloropalladium(II) is substantially insoluble in acid chloride media and may be used to precipitate palladium and, because it can be re-dissolved in excess ammonia and re-precipitated, to purify the metal in some refinery circuits. Certain platinum(II) coordination

complexes with different ligands (e.g., cisplatin or cis-diamminodichloroplatinum(II), carboplatin, and oxaliplatin) are used in cancer chemotherapy (so-called “platins”). As a ‘soft’ metal, platinum also has a great affinity for sulphur, such as with dimethyl sulfoxide (DMSO); numerous DMSO complexes have been reported (see Figure 2-3). This ability to form strong, stable complexes with amine -N and sulphur -S centres, which are present in biological macromolecules, undoubtedly influences the biological activity of certain platinum compounds,

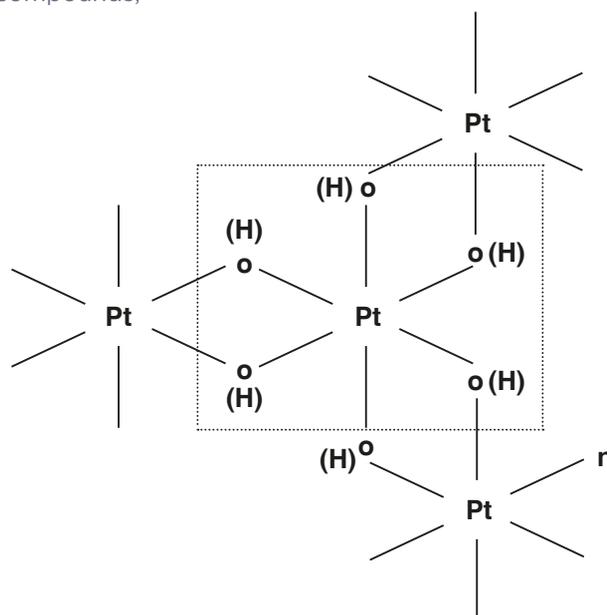
including their toxicity (see Chapter 6).

Increasingly important classes of compounds are the so-called PGM ‘nitrates’ which can be used for catalyst impregnation. These are generally formed by dissolution of the metal or an oxide/hydroxide compound in nitric acid. As with most aqueous PGM chemistry, these are not simple binary compounds and involve a range of complexes, some of which may include bridged polymeric species (see Figure 2-4).



Sulphur-bonded
trans chloromethylbis(dimethylsulphoxide)Platinum (II)

Figure 2-3: Example of a Pt-DMSO complex



Proposed oligomer of the Pt-bridged structure in ‘Pt(II) nitrate’
[Danan Dou et al., (2001) Structure and chemical properties of Pt nitrate and application in three-way automotive emission catalysts. Applied Catalysis B Environmental 30: 11-24.]

Figure 2-4: Postulated structure for a form of Pt nitrate

2.3

TABLE 2-1: PHYSICAL PROPERTIES OF PGMs AND SELECTED COMPOUNDS

The physical and mechanical properties of the platinum group metals indicate a wide range of properties with widely varying densities and solubilities. The following tables list some of the more important platinum group metal compounds found in the workplace, along with their melting points, solubility in water, and their chemical formulae.

Industry Name	Formula	Molecular Weight	Melting Point (°C)	Density (kg/m ³)	Solubility in Water
Platinum Substances					
Platinum ^a	Pt	195.09	1768.2	21.45 ^b	0.08 µ/l ^f
Platinum(II) oxide	PtO	211.08	325 ^c	14.1	Insoluble
Platinum(IV) oxide	PtO ₂	227.08	>450	11.8	0.11mg/l ^f
Platinum(IV) sulphide	PtS ₂	259.21	225-250 ^c	7.85	Insoluble
Platinum(II) chloride	PtCl ₂	265.99	581 ^c	6.0	Insoluble
Platinum(IV) chloride	PtCl ₄	336.89	327 ^c	4.30	Slightly soluble
'Platinum(II) nitrate'	Mixed Pt(IV) complexes	-	-	-	Soluble
Platinum(IV) sulphate tetrahydrate	Mixed complexes in solution	-	-	-	Soluble
Ammonium tetrachloroplatinate(II)	(NH ₄) ₂ [PtCl ₄]	372.97	- ^c	2.94	Soluble
Potassium tetrachloroplatinate(II)	K ₂ [PtCl ₄]	415.09	500 ^c	3.38	191g/l at 20°C
Hexachloroplatinic(IV) acid	H ₂ [PtCl ₆]	409.81	60 ^{d f}	2.43 ^d	1400g/l at 18°C ^d
Ammonium hexachloroplatinate(IV)	(NH ₄) ₂ [PtCl ₆]	443.87	380 ^c	3.07	5g/l at 20°C
Potassium hexachloroplatinate(IV)	K ₂ [PtCl ₆]	485.99	250 ^c	3.5	7.7g/l at 20°C
Sodium hexachloroplatinate(IV)	Na ₂ [PtCl ₆]	453.77	250 ^c	3.5	Very soluble ^d
Cis diamminedichloro-platinum(II)	[Pt(NH ₃) ₂ Cl ₂]	300.05	270 ^c	-	2.5g/l at RT
Tetraammineplatinum(II) dichloride	[Pt(NH ₃) ₄]Cl ₂	333.98	80 ^c	2.7	240g/kg

^a The boiling point of platinum metal is 3825°C.

^b At 20°C.

^c Decomposes.

^d Hexahydrate.

^e May dissolve in own water of crystallization..

^f By transformation/dissolution kinetics tests at 100mg/l after 7 days.

RT = Room Temperature.

- = No data.

2.3

TABLE 2-1: PHYSICAL PROPERTIES OF PGMs AND SELECTED COMPOUNDS

Industry Name	Formula	Molecular Weight	Melting Point (°C)	Density (kg/m ³)	Solubility in Water
Palladium Substances					
Palladium	Pd	106.4	1554.8	12.0	<0.01 µg/l ^f
Palladium(II) oxide	PdO	122.40	750 ^c	8.7	<0.01mg/l
Palladium(II) dichloride	PdCl ₂	177.33	679 ^c	4.0	4g/l at RT
Palladium(II) dibromide	PdBr ₂	266.22	500	-	Insoluble
Palladium(II) diiodide	PdI ₂	360.21	350 ^c	6	Insoluble
Palladium diacetate	Pd(C ₂ H ₃ O ₂) ₂	225	200 ^c	-	Insoluble
Palladium(II) acetate Trimer	{Pd(C ₂ H ₃ O ₂) ₂ } ₃	673.53	-	-	0.35g/l at 20°C
Palladium(II) sulphate	Mixed complexes in solution	-	125 ^c	-	280g/l
'Palladium(II) nitrate'	Mixed Pd(II) complexes	-	Decomposes	-	>10g/l
Diammonium hexachloropalladate(IV)	(NH ₄) ₂ [PdCl ₆]	355.22	240 ^c	-	>10g/l at RT
Potassium hexachloropalladate(IV)	K ₂ [PdCl ₆]	397.3	>450	2.7	3.41g/l at RT
Dipotassium tetrachloropalladate	K ₂ [PdCl ₄]	326.4	524	2.7	Soluble
Disodium tetrachloropalladate(II)	Na ₂ [PdCl ₄]	294.21	395 ^c	-	622g/l
Diamminedinitro-palladium(II)	Pd(NO ₂) ₂ (NH ₃) ₂	232.5	230	-	Slightly soluble
Trans diamminedichloro- palladium(II)	PdCl ₂ (NH ₃) ₂	211.39	323 ^c	-	0.63g/l at RT
Tetraamminepalladium(II) dichloride	[Pd(NH ₃) ₄]Cl ₂	263.5	300 ^c	1.91	327g/l
Tetraamminepalladium(II) hydrogen carbonate	[Pd(NH ₃) ₄](HCO ₃) ₂	296.6	-	-	56.2g/l at 20°C
Dihydrogen tetrachloropalladate(II)	H ₂ [PdCl ₄]	250.2	-	-	-
Bis(acetylacetonato) palladium(II)	Pd(C ₅ H ₇ O ₂) ₂	304.64	180 ^c	-	0.011mg/l
Bis(dibenzylidene-acetone) palladium(0)	Pd(C ₁₇ H ₁₄ O)	575.02	150	-	-
Dichlorobis(triphenyl)-phosphine palladium(II)	PdCl ₂ [(C ₆ H ₅) ₃ P] ₂	701.90	254 ^c	-	<7x10 ⁻⁵ g/l at 20°C
Dichloro(1,5-cyclooctadiene) palladium(II)	PdCl ₂ (C ₈ H ₁₂)	285.51	210 ^c	-	-

^a The boiling point of platinum metal is 3825°C.^b At 20°C.^c Decomposes.^d Hexahydrate.^e May dissolve in own water of crystallization..^f By transformation/dissolution kinetics tests at 100mg/l after 7 days.

RT = Room Temperature.

- = No data.

2.3

TABLE 2-1: PHYSICAL PROPERTIES OF PGMs AND SELECTED COMPOUNDS

Industry Name	Formula	Molecular Weight	Melting Point (°C)	Density (kg/m ³)	Solubility in Water
Rhodium Substances					
Rhodium	Rh	102.91	1960	12.41	<0.1 µ/l ^f
Rhodium(III) oxide	Rh ₂ O ₃	253.81	1100 ^c	8.2	0.5 µ/l ^f
Rhodium(III) trichloride	RhCl ₃	209.26	-	-	Insoluble
Rhodium(III) trichloride, hydrated	Mixed complexes	-	>450°C	-	696g/l
'Rhodium(III) nitrate'	Mixed complexes	-	<160 ^c	-	1170g/l at RT
Rhodium(III) sulphate	Rh ₂ (SO ₄) ₃ •12H ₂ O Mixed complexes in solution.	-	>500°C	-	>100g/l
Rhodium(III) chloropentaammine dichloride	Rh[Cl(NH ₃) ₅]Cl ₂	294.42	-	-	Low solubility
Triammonium hexachlororhodate(III)	(NH ₄) ₃ [RhCl ₆]	369.74	260 ^c	-	99.8g/l at RT
Tris(triphenylphosphine) rhodium(I) chloride	[RhCl{P(C ₆ H ₅) ₃ } ₃]	925.23	103 ^c	-	<1x10 ⁻⁴ g/l
Carbonyltrihydrido (triphenylphosphine) rhodium(I)	[RhH(CO){P(C ₆ H ₅) ₃ } ₃]	918.19	97 ^c	-	6x10 ⁻⁶ g/l at 20°C
Ruthenium Substances					
Ruthenium	Ru	101.7	2334	12.45	0.02 µ/l ^f
Ruthenium(II) dichloride	RuCl ₂	171.98	-	-	Insoluble
Ruthenium(III) trichloride	RuCl ₃	207.43	-500 ^c	-	Insoluble
Ruthenium(III) trichloride hydrated	Mixed complexes	-	90 ^c	-	1140g/l at RT
Ruthenium tetrachloride	RuCl ₄	242.88	-	-	Slightly soluble
Ruthenium(IV) dioxide, hydrated	RuO ₂ •xH ₂ O	-	1300 ^c	7.05	0.08 µ/l ^f
Ruthenium(VIII) tetroxide	RuO ₄	164.7	25	-	Decomposes
Diammonium hexachlororuthenate(IV)	(NH ₄) ₂ [RuCl ₆]	349.87	320 ^c	2.21	>22.6g/l (may hydrolyse)
Tris(nitrate-O) nitrosylruthenium(III)	[Ru(NO ₃) ₃ (NO)]	317.09	140 ^c	-	690g/l
Dichlorotris(triphenyl-phosphine) ruthenium(II)	[RuCl ₂ {P(C ₆ H ₅) ₃ } ₂]	958.83	116 ^c	-	<4x10 ⁻⁵ g/l at 20°C

^a The boiling point of platinum metal is 3825°C.^b At 20°C.^c Decomposes.^d Hexahydrate.^e May dissolve in own water of crystallization..^f By transformation/dissolution kinetics tests at 100mg/l after 7 days.

RT = Room Temperature.

- = No data.

2.3

TABLE 2-1: PHYSICAL PROPERTIES OF PGMs AND SELECTED COMPOUNDS

Industry Name	Formula	Molecular Weight	Melting Point (°C)	Density (kg/m ³)	Solubility in Water
Osmium Substances					
Osmium	Os	190.2	3050	22.61	Insoluble
Osmium dioxide	OsO ₂	222.2	-	7.91	Insoluble
Osmium(VIII) tetroxide	OsO ₄	254.20	40	4.91	72g/l
Osmium dichloride	OsCl ₂	261.11	-	-	Soluble, decomposes
Iridium Substances					
Iridium	Ir	192.22	2446	22.56	<0.01 μ/l ^f
Iridium dioxide	IrO ₂	224.20	1100 ^c	11.7	0.0002g/l at RT
Iridium(III) trichloride	IrCl ₃	298.58	763 ^c	-	Insoluble
Iridium(III) trichloride, hydrated	IrCl ₃ .xH ₂ O, mixed complexes	-	-	5.3	220g/l
Dihydrogen-hexachloroiridate(IV)	H ₂ [IrCl ₆].6H ₂ O	515.04	80 ^c	-	456g/l
Diammonium hexachloroiridate(IV)	(NH ₄) ₂ [IrCl ₆]	441.01	60 ^c	2.86	-
Di-μ-chlorobis((1,2,5,6-eta)cycloocta-1,5-diene))diiridium(I)	[IrCl(C ₈ H ₁₂)] ₂	671.71	202 ^c	-	-

^a The boiling point of platinum metal is 3825°C.^b At 20°C.^c Decomposes.^d Hexahydrate.^e May dissolve in own water of crystallization..^f By transformation/dissolution kinetics tests at 100mg/l after 7 days.

RT = Room Temperature.

- = No data.

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