

																1	2																
																H	He																
3	4											5	6	7	8	9	10																
Li	Be											B	C	N	O	F	Ne																
11	12											13	14	15	16	17	18																
Na	Mg											Al	Si	P	S	Cl	Ar																
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																
55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72																
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104																
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub																						
																		105	106	107	108	109	110	111	112	113	114	115	116	117	118		
																		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Th	Dy	Ho	Er	Tm	Yb	Lu		
																		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

26

Cobalt, Rhodium and Iridium

26.1 Introduction

Although hardly any metallic cobalt was used until the twentieth century, its ores have been used for thousands of years to impart a blue colour to glass and pottery. It is present in Egyptian pottery dated at around 2600 BC and Iranian glass beads of 2250 BC.[†] The source of the blue colour was recognized in 1735 by the Swedish chemist G. Brandt, who isolated a very impure metal, or “regulus”, which he named “cobalt rex”. In 1780 T. O. Bergman showed this to be a new element. Its name has some resemblance to the Greek word for “mine” but is almost certainly derived from the German word *Kobold* for “goblin” or “evil spirit”. The miners of northern European countries thought that the spitefulness of such spirits was responsible for ores which, on smelting, not only failed

unexpectedly to yield the anticipated metal but also produced highly toxic fumes (As_4O_6).

In 1803 both rhodium and iridium were discovered⁽¹⁾, like their preceding neighbours in the periodic table, ruthenium and osmium, in the black residue left after crude platinum had been dissolved in aqua regia. W. H. Wollaston discovered rhodium, naming it after the Greek word $\rho\acute{o}\delta\omicron\nu$ for “rose” because of the rose-colour commonly found in aqueous solutions of its salts. S. Tennant discovered iridium along with osmium, and named it after the Greek goddess Iris ($i\rho\iota\varsigma, i\rho\iota\delta-$), whose sign was the rainbow, because of the variety of colours of its compounds.

26.2 The Elements

26.2.1 Terrestrial abundance and distribution

Rhodium and iridium are exceedingly rare elements, comprising only 0.0001 and 0.001 ppm of the earth’s crust respectively, and even

[†] “Smalt”, produced by fusing potash, silica and cobalt oxide, can be used for colouring glass or for glazing pottery. The secret of making this brilliant blue pigment was apparently lost, to be rediscovered in the fifteenth century. Leonardo da Vinci was one of the first to use powdered smalt as a “new” pigment when painting his famous “The Madonna of the Rocks”.

¹ L. B. HUNT, *Platinum Metals Rev.* **31**, 32–41 (1987).

cobalt (29 ppm, i.e. 0.0029%), though widely distributed, stands only thirtieth in order of abundance and is less common than all other elements of the first transition series except scandium (25 ppm).

More than 200 ores are known to contain cobalt but only a few are of commercial value. The more important are arsenides and sulfides such as smaltite, CoAs_2 , cobaltite (or cobalt glance), CoAsS , and linnaeite, Co_3S_4 . These are invariably associated with nickel, and often also with copper and lead, and it is usually obtained as a byproduct or coproduct in the recovery of these metals. The world's major sources of cobalt are the African continent and Canada with smaller reserves in Australia and the former USSR. All the platinum metals are generally associated with each other and rhodium and iridium therefore occur wherever the other platinum metals are found. However, the relative proportions of the individual metals are by no means constant and the more important sources of rhodium are the nickel-copper-sulfide ores found in South Africa and in Sudbury, Canada, which contain about 0.1% Rh. Iridium is usually obtained from native osmiridium ($\text{Ir} \sim 50\%$) or iridosmium ($\text{Ir} \sim 70\%$) found chiefly in Alaska as well as South Africa.

26.2.2 Preparation and uses of the elements⁽²⁾

The production of cobalt^(2,3) is usually subsidiary to that of copper and nickel and the methods employed differ widely, depending on which of these it is associated with. In general the ore is subjected to appropriate roasting treatment so as to remove gangue material as a slag and produce a "speiss" of mixed metal and oxides. In the case of arsenical ores, As_2O_6 is condensed and provides a valuable byproduct. In the case of copper ores, the primary process

leaves a spent electrolyte from which iron is precipitated as the hydroxide by lime and the cobalt then separated by further electrolysis. Nickel ores yield acidic sulfate or chloride solutions and the methods used to separate the nickel and cobalt include: (a) precipitation of cobalt as the sulfide; (b) oxidation of cobalt and precipitation of $\text{Co}(\text{OH})_3$; (c) making the solution alkaline with NH_3 and removal of nickel either as the sparingly soluble $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ or by selective reduction to the metal by H_2 under pressure; (d) anion exchange, utilizing the preferential formation of $[\text{CoCl}_4]^{2-}$.

World production of cobalt in 1995 was about 20 000 tonnes, considerably below capacity. The major producing countries are Zaire, Zambia, Canada, Finland and the former Soviet Union.

The largest use of cobalt is in the production of chemicals for the ceramic and paint industries. In ceramics the main use now is not to provide a blue colour, but rather white by counterbalancing the yellow tint arising from iron impurities. Blue pigments are, however, used in paints and inks, and cobalt compounds are used to hasten the oxidation and hence the drying of oil-based paints. Cobalt compounds are also employed as catalysts in a range of organic reactions of which the "OXO" (or hydroformylation) reaction and hydrogenation and dehydrogenation reactions are the most important (pp. 1134–6).

Other uses include the manufacture of magnetic alloys. Of these the best known is "Alnico", a steel containing, as its name implies, aluminium and nickel, as well as cobalt. It is used for permanent magnets which are up to 25 times more powerful than ordinary steel magnets.

As already noted (p. 1073), the platinum metals are all isolated from concentrates obtained as "anode slimes" or "converter matte." In the classical process, after ruthenium and osmium have been removed, excess oxidants are removed by boiling, iridium is precipitated as $(\text{NH}_4)_2\text{IrCl}_6$ and rhodium as $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. In alternative solvent extraction processes (p. 1147) $[\text{IrCl}_6]^{2-}$ is extracted in organic amines leaving rhodium in the aqueous phase to be precipitated, again, as $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. In all cases ignition in H_2

² J. HILL, Chap. 2 in D. THOMPSON (ed.), *Insights into Speciality Inorganic Chemicals*, pp. 5–34, R.S.C., Cambridge, 1995.

³ *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., Vol. 6, pp. 760–77, Interscience New York, 1993.

yields the metals as powders or sponges which can be consolidated by the techniques of powder metallurgy.

In 1996, consumption in the western world was 14.2 tonnes of rhodium and 3.8 tonnes of iridium. Unquestionably the main uses of rhodium (over 90%) are now catalytic, e.g. for the control of exhaust emissions in the car (automobile) industry and, in the form of phosphine complexes, in hydrogenation and hydroformylation reactions where it is frequently more efficient than the more commonly used cobalt catalysts. Iridium is used in the coating of anodes in chloralkali plant and as a catalyst in the production of acetic acid. It also finds small-scale applications in specialist hard alloys.

26.2.3 Properties of the elements

Some of the important properties of these three elements are summarized in Table 26.1.

The metals are lustrous and silvery with, in the case of cobalt, a bluish tinge. Rhodium and iridium are both hard, cobalt less so but still appreciably harder than iron. Rhodium and Ir have fcc structures, the first elements in the transition series to do so; this is in keeping

with the view, based on band-theory calculations, that the fcc structure is more stable than either bcc or hcp when the outer d orbitals are nearly full. Cobalt, too, has an allotrope (the β -form) with this structure but this is only stable above 417°C; below this temperature the hcp α -form is the more stable. However, the transformation between these allotropes is generally slow and the β -form, which can be stabilized by the addition of a few per cent of iron, is often present at room temperature. This, of course, has an effect on physical properties and is no doubt responsible for variations in reported values for some properties even in the case of very pure cobalt. By contrast the atomic weights of cobalt and rhodium at least are known with considerable precision, since these elements each have but one naturally occurring isotope. In the case of cobalt this is ^{59}Co , but bombardment by thermal neutrons converts this to the radioactive ^{60}Co . The latter has a half-life of 5.271 y and decays by means of β^- and γ emission to non-radioactive ^{60}Ni . It is used in many fields of research as a concentrated source of γ -radiation, and also medically in the treatment of malignant growths. Iridium has two stable isotopes: ^{191}Ir 37.3% and ^{193}Ir 62.7%.

Table 26.1 Some properties of the elements cobalt, rhodium and iridium

Property	Co	Rh	Ir
Atomic number	27	45	77
Number of naturally occurring isotopes	1	1	2
Atomic weight	58.933200(9)	102.90550(2)	192.217(3)
Electronic configuration	[Ar]3d ⁷ 4s ²	[Kr]4d ⁸ 5s ¹	[Xe]4f ¹⁴ 5d ⁷ 6s ²
Electronegativity	1.8	2.2	2.2
Metal radius (12-coordinate)/pm	125	134	135.5
Effective ionic radius (6-coordinate)/pm			
	V	55	57
	IV	60	62.5
	III	66.5	68
	II	—	—
MP/°C	1495	1960	2443
BP/°C	3100	3760	4550(±100)
$\Delta H_{\text{fus}}/\text{kJ mol}^{-1}$	16.3	21.6	26.4
$\Delta H_{\text{vap}}/\text{kJ mol}^{-1}$	382	494	612(±13)
$\Delta H_{\text{f}}(\text{monatomic gas})/\text{kJ mol}^{-1}$	425(±17)	556(±11)	669(±8)
Density (20°C)/g cm ⁻³	8.90	12.39	22.56
Electrical resistivity (20°C)/ $\mu\text{ohm cm}$	6.24	4.33	4.71

The mps, bps and enthalpies of atomization are lower than for the preceding elements in the periodic tables, presumably because the $(n - 1)d$ electrons are being drawn increasingly into the inert electron cores of the atoms. In the first series Co, like its neighbours Fe and Ni, is ferromagnetic (in both allotropic forms); while it does not attain the high saturation magnetization of iron, its Curie point ($>1100^\circ\text{C}$) is much higher than that for Fe (768°C).

26.2.4 Chemical reactivity and trends

Cobalt is appreciably less reactive than iron, and so contrasts less markedly with the two heavier members of its triad. It is stable to atmospheric oxygen unless heated, when it is oxidized first to Co_3O_4 ; above 900°C the product is CoO which is also produced by the action of steam on the red-hot metal. It dissolves rather slowly in dil mineral acids giving salts of Co^{II} , and reacts on heating with the halogens and other non-metals such as B, C, P, As and S, but is unreactive to H_2 and N_2 .

Rhodium and iridium will also react with oxygen and halogens at red-heat, but only slowly, and these metals are especially notable for their extreme inertness to acids, even aqua regia. Dissolution of rhodium metal is best effected by fusion with NaHSO_4 , a process used in its commercial separation. In the case of iridium, oxidizing molten alkalis such as Na_2O_2 or $\text{KOH} + \text{KNO}_3$ will produce IrO_2 which can then be dissolved in aqua regia. Alternatively, a rather extreme measure which is efficacious with both metals, is to heat them with conc $\text{HCl} + \text{NaClO}_3$ in a sealed tube at $125\text{--}150^\circ\text{C}$.

Table 26.2 is a list of examples of compounds of these elements in various oxidation states. The most striking feature of this, as compared to the corresponding lists for preceding triads, is that for the first time the range of oxidation states has diminished. This is a manifestation of the increasing stability of the $(n - 1)d$ electrons, whose attraction to the atomic nucleus is now sufficient to prevent the elements attaining the highest oxidation states and so to render irrelevant the concept of a "group" oxidation

state. No oxidation states are found above $+6$ for Rh and Ir, or above $+5$ for Co. Indeed, examples of cobalt in $+4$ and $+5$ and of rhodium or iridium in $+5$ and $+6$ oxidation states are rare and sometimes poorly characterized.

The most common oxidation states of cobalt are $+2$ and $+3$. $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ are both known but the latter is a strong oxidizing agent and in aqueous solution, unless it is acidic, it decomposes rapidly as the Co^{III} oxidizes the water with evolution of oxygen. Consequently, in contrast to Co^{II} , Co^{III} provides few simple salts, and those which do occur are unstable. However, Co^{III} is unsurpassed in the number of coordination complexes which it forms, especially with N -donor ligands. Virtually all of these complexes are low-spin, the t_{2g}^6 configuration producing a particularly high CFSE (p. 1131).

The effect of the CFSE is expected to be even more marked in the case of the heavier elements because for them the crystal field splittings are much greater. As a result the $+3$ state is the most important one for both Rh and Ir and $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ are the only simple aquo ions formed by these elements. With π -acceptor ligands the $+1$ oxidation state is also well known for Rh and Ir. It is noticeable, however, that the similarity of these two heavier elements is less than is the case earlier in the transition series and, although rhodium resembles iridium more than cobalt, nevertheless there are significant differences. One example is provided by the $+4$ oxidation state which occurs to an appreciable extent in iridium but not in rhodium. (The ease with which $\text{Ir}^{\text{IV}} \rightleftharpoons \text{Ir}^{\text{III}}$ sometimes occurs can be a source of annoyance to preparative chemists.)

Table 26.2 also reveals a diminished tendency on the part of these elements to form compounds of high coordination number when compared with the iron group and, apart from $[\text{Co}(\text{NO}_3)_4]^{2-}$, a coordination number of 6 is rarely exceeded. There is also a marked reluctance to form oxoanions (p. 1118). This is presumably because their formation requires the donation of π electrons from the oxygen atoms to the metal and the metals become progressively

Table 26.2 Oxidation states and stereochemistries of some compounds of cobalt, rhodium and iridium

Oxidation state	Coordination number	Stereochemistry	Co	Rh/Ir
-3	3		[Co(CO) ₃] ³⁻	[M(CO) ₃] ³⁻
-1 (d ¹⁰)	4	Tetrahedral	[Co(CO) ₄] ⁻	[Rh(CO) ₄] ⁻ , [Ir(CO) ₃ (PPh ₃)] ⁻
0 (d ⁹)	4	Tetrahedral	[Co(PMe ₃) ₄]	
	6	Octahedral	[Co ₂ (CO) ₈]	[M ₄ (CO) ₁₂]
1 (d ⁸)	2	Linear	[CoO ₂] ³⁻	
	3	Planar (?)		[RhCl(PCy ₃) ₂]
		T-shaped		[Rh(PPh ₃) ₃] ⁺
	4	Square planar		[RhCl(PPh ₃) ₃] [Ir(CO)Cl(PPh ₃) ₂]
	5	Trigonal bipyramidal	[Co(NCMe) ₅] ⁺	[RhH(PF ₃) ₄], [Ir(CO)H(PPh ₃) ₃]
		Square pyramidal	[Co(NCPh) ₅] ⁺	
	6	Octahedral	[Co(bipy) ₃] ⁺	
2 (d ⁷)	2	Linear	[Co{N(SiMe ₃) ₂] ₂]	
	3	Planar	[Co{N(SiMe ₃) ₂] ₂ (PPh ₃)]	
	4	Tetrahedral	[CoCl ₄] ²⁻	
		Square planar	[Co(phthalocyanine)]	[RhCl ₂ {P(<i>o</i> -MeC ₆ H ₄) ₃] ₂]
	5	Trigonal bipyramidal	[CoBr{N(C ₂ H ₄ NMe ₂) ₃ }] ⁺	
		Square pyramidal	[Co(CN) ₅] ³⁻	[Rh ₂ (O ₂ CMe) ₄]
	6	Octahedral	[Co(H ₂ O) ₆] ²⁺	[Rh ₂ (O ₂ CMe) ₄ (H ₂ O) ₂]
	8	Dodecahedral	[Co(NO ₃) ₄] ²⁻	
3 (d ⁶)	4	Tetrahedral	[CoW ₁₂ O ₄₀] ⁵⁻	
	5	Trigonal bipyramidal		[IrH ₃ (PR ₃) ₂]
		Square pyramidal	[Co(corrole)(PPh ₃)] ^(a)	[RhI ₂ Me(PPh ₃) ₂]
	6	Octahedral	[Co(NH ₃) ₆] ³⁺	[MCl ₆] ³⁻
4 (d ⁵)	4	Tetrahedral	[Co(1-norbornyl) ₄] ^(b)	
	6	Octahedral	[CoF ₆] ²⁻	[MCl ₆] ²⁻
5 (d ⁴)	6	Octahedral		[MF ₆] ⁻
	7	Pentagonal bipyramidal		[IrH ₅ (PR ₃) ₂]
6 (d ³)	6	Octahedral		[MF ₆]

^(a)Corrole is a tetrapyrrolic macrocycle

^(b)1-Norbornyl is a bicyclo[2.2.1]hept-1-yl

less able to act as π acceptors as their d orbitals are filled.

Hydrido complexes of all three elements, and covering a range of formal oxidation states, are important because of their roles in homogeneous catalysis either as the catalysts themselves or as intermediates in the catalytic cycles.

26.3 Compounds of Cobalt, Rhodium and Iridium

Binary borides (p. 147) and carbides (p. 297) have been discussed already.

26.3.1 Oxides and sulfides

As a result of the diminution in the range of oxidation states which has already been mentioned, the number of oxides formed by these elements is less than in the preceding groups, being confined to two each for cobalt (CoO, Co₃O₄) and rhodium (Rh₂O₃, RhO₂) and to just one for iridium (IrO₂) (though an impure sesquioxide Ir₂O₃ has been reported — see below). No trioxides are known.

The only oxide formed by any of these metals in the divalent state is CoO; this is prepared as an olive-green powder by strongly heating the metal in air or steam, or alternatively by heating

the hydroxide, carbonate or nitrate in the absence of air. It has the rock-salt structure and is anti-ferromagnetic below 289 K. By reacting it with silica and alumina, pigments are produced which are used in the ceramics industry. CoO is stable in air at ambient temperatures and above 900°C but if heated at, say, 600–700°C, it is converted into the black Co₃O₄. This is Co^{II}Co^{III}₂O₄ and has the normal spinel structure with Co^{II} ions in tetrahedral and Co^{III} in octahedral sites within the ccp lattice of oxide ions. This is to be expected (p. 1080) because of the dominating advantage of placing the d⁶ ions in octahedral sites, where adoption of the low-spin configuration gives it a decisively favourable CFSE. The ability of Co₃O₄ to absorb oxygen, and possibly also the retention of water in preparations from the hydroxide, have led to claims for the existence of Co₂O₃, but it is doubtful if these claims are valid. Oxidation of Co(OH)₂, or addition of aqueous alkali to a cobalt(III) complex, produces a dark-brown material which on drying at 150°C in fact gives cobalt(III) oxide hydroxide, CoO(OH).

Heating rhodium metal or the trichloride in oxygen at 600°C, or simply heating the trinitrate, produces dark-grey Rh₂O₃ which has the corundum structure (p. 242); it is the only stable oxide formed by this metal. The yellow precipitate formed by the addition of alkali to aqueous solutions of rhodium(III) is actually Rh₂O₃·5H₂O rather than a genuine hydroxide. Electrolytic oxidation of Rh^{III} solutions and addition of alkali gives a yellow precipitate of RhO₂·2H₂O, but attempts to dehydrate this produce Rh₂O₃. Black anhydrous RhO₂ is best obtained by heating Rh₂O₃ in oxygen under pressure; it has the rutile structure, but it is not well characterized.

For iridium the position is reversed. This time it is the black dioxide, IrO₂, with the rutile structure (p. 961), which is the only definitely established oxide. It is obtained by heating the metal in oxygen or by dehydrating the precipitate produced when alkali is added to an aqueous solution of [IrCl₆]²⁻. Contamination either by unreacted metal or by alkali is, however, difficult to avoid. The other oxide, Ir₂O₃, is said to be

obtained by igniting K₂IrCl₆ with NaCO₃ or, as its hydrate, by adding KOH to aqueous K₃[IrCl₆] under CO₂. However, even if it is a true compound, it is always impure and is readily oxidized to IrO₂.

Oxoanions are rare in this group; exceptions include the unstable [Co^VO₄]³⁻ and [Co^{II}O₃]⁴⁻. Heating mixtures of the appropriate oxides in oxygen, or under pressure, produces materials with the stoichiometry, M₃CoO₄, which, together with their oxidizing properties, suggests the presence of Co^V. When CoO is heated with 2.2 moles of Na₂O at 550° in a sealed tube under argon, bright-red crystals of Na₄Co^{II}O₃ are formed. The compound hydrolyses immediately on contact with atmospheric moisture and is notable in containing discrete planar [CoO₃]⁴⁻ ions reminiscent of the carbonate ion (Co–O 186 ± 6 pm) and is similar to the red oxoferrate(II), Na₄[FeO₃]. The lustrous red tetracobaltate(II) Na₁₀[Co^{II}₄O₉], with an anion analogous to the *catena*-tetracarbonate [C₄O₉]²⁻, is also known. For iridium, prolonged heating of IrO₂ and Li₂O produces Li₂IrO₃ which, when heated with 2.2 moles of Na₂O at 800°C for 71 days, gives transparent red crystals of Na₄IrO₄ in which the Ir(IV) is surrounded by four O²⁻ in a square (Ir–O = 190.2 pm.)⁽⁴⁾

A larger number of sulfides have been reported but not all of them have been fully characterized. Cobalt gives rise to CoS₂ with the pyrites structure (p. 680), Co₃S₄ with the spinel structure (p. 247), and Co_{1-x}S which has the NiAs structure (p. 555) and is cobalt-deficient. All are metallic, as is Co₉S₈ and the corresponding selenides and tellurides. The sulfides of rhodium and iridium are notable mainly for their inertness especially towards acids, and most of them are semiconductors. They are the disulfides MS₂, obtained from the elements; the “sesquisulfides” M₂S₃, obtained by passing H₂S through aqueous solutions of M^{III}; and Rh₂S₅ and IrS₃, obtained by heating MCl₃ + S at 600°C. Numerous nonstoichiometric selenides and tellurides are also known.

⁴ K. MADERAND and R. HOPPE, *Z. anorg. allg. Chem.* **619**, 1647–54 (1993).

Table 26.3 Halides of cobalt, rhodium and iridium (mp/°C)

Oxidation state	Fluorides	Chlorides	Bromides	Iodides
+6	RhF ₆ black (70°) IrF ₆ yellow (44°) bp 53°			
+5	[RhF ₅] ₄ dark red [IrF ₅] ₄ yellow (104°)			
+4	CoF ₄ RhF ₄ purple-red IrF ₄ dark brown	IrCl ₄ ?	IrBr ₄ ?	IrI ₄ ?
+3	CoF ₃ light brown RhF ₃ red IrF ₃ black	RhCl ₃ red IrCl ₃ red	RhBr ₃ red-brown IrBr ₃ red-brown	RhI ₃ black IrI ₃ dark brown
+2	CoF ₂ pink (1200°)	CoCl ₂ blue (724°)	CoBr ₂ green (678°)	CoI ₂ a blue-black (515°)

Because of possible catalytic and biological relevance of metal–sulfur clusters, several such compounds of cobalt have been prepared. The action of H₂S or M₂S (M = alkali metal) on a non-aqueous solution of a convenient cobalt compound (often containing, or in the presence of, a phosphine) is a typical route. Diamagnetic [Co₆S₈(PR₃)₆] (R = Et, Ph) comprise an octahedral array of metal atoms (Co–Co in the range 281.7 to 289.4 pm), all faces capped by μ₃-S atoms,⁽⁵⁾ and show facile redox behaviour



An indication of the range of such clusters which might possibly be synthesized is given by the observation⁽⁶⁾ that mass spectroscopic analysis of the products of laser-ablation of CoS

show no less than 83 gaseous ions ranging from [CoS₂]⁻ to [Co₃₈S₂₄]⁻.

26.3.2 Halides

The known halides of this triad are listed in Table 26.3. It can be seen that, apart from CoF₃, CoF₄ and the doubtful iridium tetrahalides, they fall into three categories:

- higher fluorides of Ir and Rh;
- a full complement of trihalides of Ir and Rh;
- dihalides of cobalt

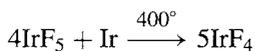
The octahedral hexafluorides are obtained directly from the elements and both are volatile, extremely reactive and corrosive solids, RhF₆ being the least stable of the platinum metal hexafluorides and reacting with glass even when carefully dried. They are thermally unstable and must be frozen out from the hot gaseous reaction mixtures, otherwise they dissociate.

⁵ M. HONG, Z. HUANG, X. LEI, G. WEI, B. KANG and H. LIU, *Polyhedron*, **10**, 927–34 (1991).

⁶ J. EL NAKAT, K. J. FISHER, I. G. DANCE and G. D. WILLET, *Inorg. Chem.* **32** 1931–40 (1993).

The pentafluorides of Rh and Ir may be prepared by the deliberate thermal dissociation of the hexafluorides. They also are highly reactive and are respectively dark-red and yellow solids, with the same tetrameric structure as $[\text{RuF}_5]_4$ and $[\text{OsF}_5]_4$ (p. 1083).

RhF_4 is a purple-red solid, usually prepared by the reaction of the strong fluorinating agent BrF_3 on RhBr_3 . The corresponding compound IrF_4 has had an intriguing and instructive history.⁽⁷⁾ It was first claimed in 1929 and again in 1956 but this material was shown in 1965 to be, in reality, the previously unknown IrF_5 . IrF_4 can now be made (1974) by reducing IrF_5 with the stoichiometric amount of iridium-black:



The dark-brown product disproportionates above 400° into IrF_3 and the volatile IrF_5 . The structure features $\{\text{IrF}_6\}$ octahedra which share 4 F atoms, each with one other $\{\text{IrF}_6\}$ group, leaving a pair of *cis* vertices unshared: this is essentially a rutile type structure (p. 961) from which alternate metal atoms have been removed from each edge-sharing chain. It was the first 3D structure to have been found for a tetrafluoride.⁽⁷⁾ Claims have been made for the isolation of all the other iridium tetrahalides, but there is some doubt as to whether these can be substantiated. This is an unexpected situation since +4 is one of iridium's common oxidation states and, indeed, the derived anions $[\text{IrX}_6]^{2-}$ ($X = \text{F}, \text{Cl}, \text{Br}$) are well known.

The most familiar and most stable of the halides of Rh and Ir, however, are the trihalides. Those of Rh range in colour from the red RhF_3 to black RhI_3 and, apart from the latter, which is obtained by the action of aqueous KI on the tribromide, they may be obtained in the anhydrous state directly from the elements. RhF_3 has a structure similar to that of ReO_3 (p. 1047), while RhCl_3 is isomorphous with AlCl_3 (p. 234). The anhydrous trihalides are generally unreactive and insoluble in water but, excepting the triiodide which is only known in this form,

water-soluble hydrates can be produced by wet methods. $\text{RhF}_3 \cdot 6\text{H}_2\text{O}$ and $\text{RhF}_3 \cdot 9\text{H}_2\text{O}$ can be isolated from aqueous solutions of Rh^{III} acidified with HF. Their aqueous solutions are yellow, possibly due to the presence of $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$. The dark-red deliquescent $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ is the most common compound of rhodium and the usual starting point for the preparation of other rhodium compounds, and is itself best prepared from the metal sponge. This is heated with KCl in a stream of Cl_2 and the product extracted with water. The solution contains $\text{K}_2[\text{Rh}(\text{H}_2\text{O})\text{Cl}_5]$ and treatment with KOH precipitates the hydrous Rh_2O_3 which can be dissolved in hydrochloric acid and the solution evaporated to dryness. $\text{RhBr}_3 \cdot 2\text{H}_2\text{O}$ also is formed from the metal by treating it with hydrochloric acid and bromine.

The iridium trihalides are rather similar to those of rhodium. Anhydrous IrF_3 is obtained by reducing IrF_6 with the metal, IrCl_3 and IrBr_3 by heating the elements, and IrI_3 by heating its hydrate *in vacuo*. Water-soluble hydrates of the tri-chloride, -bromide, and -iodide are produced by dissolving hydrous Ir_2O_3 in the appropriate acid and, like its rhodium analogue, $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ provides a convenient starting point in iridium chemistry.

Lower halides of Rh and Ir have been reported and, whilst their existence cannot be denied with certainty, further substantiation is needed. Unquestionably, the divalent state is the preserve of cobalt. Apart from the strongly oxidizing CoF_3 (a light-brown powder isomorphous with FeCl_3 and the product of the action of F_2 on CoCl_2 at 250°C) and CoF_4 (identified⁽⁸⁾ in the gaseous phase by mass spectrometry, as the singly charged cation, when CoF_3 and TbF_4 are heated to 600–680 K), the only known halides of cobalt are the dihalides. In all of these the cobalt is octahedrally coordinated. The anhydrous compounds are prepared by dry methods: CoF_2 (pink) by heating CoCl_2 in HF; CoCl_2 (blue) and CoBr_2 (green) by the action of the halogens on the heated metal; CoI_2 (blue-black) by the action

⁷ N. BARTLETT and A. TRESSAUD, *Comptes Rendus* **278C**, 1501–4 (1974).

⁸ M. V. KOBOROV, L. N. SAVINOVA and L. N. SIDEROV, *J. Chem. Thermodynam.* **25**, 1161–8 (1993).