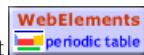


Cobalt Chemistry

History

The [origin of the name Cobalt](#) is thought to be from the German kobold for "evil spirits or goblins", who were superstitiously thought to cause trouble for miners, since the mineral contained arsenic which injured their health and the metallic ores did not yield metals when treated with the normal methods. The name could also be derived from the Greek kabalos for "mine". Cobalt was discovered in 1735 by the Swedish chemist Georg Brandt.



An excellent site for finding the properties of the elements, including cobalt is at

Occurrence

The principal ores of Cobalt are cobaltite, [(Co,Fe)AsS], erythrite, [Co₃(AsO₄)₂·8(H₂O)], glaucodot, [(Co,Fe)AsS], and skutterudite, [CoAs₃]. World production of cobalt has steadily increased in recent years, almost trebling since 1993. The dominance of African copper-cobalt producers has been replaced by a more even spread of output between leading producing countries, with Canada, Norway and more recently Australia, together with exports from Russia, replacing lost production in the Democratic Republic of Congo (Zaire). The strongest growth in production of cobalt has come in Finland, where output grew at over 16% between 1990 and 2002.

Extraction

Uses

- Alloys, such as:
 - Superalloys, for parts in gas turbine aircraft engines.
 - Corrosion- and wear-resistant alloys. Estimated as about 20% of production in 2003
- High-speed steels.
- Cemented carbides (also called hard metals) and diamond tools.
- Magnets and magnetic recording media.
- Catalysts for the petroleum and chemical industries.
- electroplating because of its appearance, hardness, and resistance to oxidation.
- Drying agents for paints, varnishes, and inks.
- Ground coats for porcelain enamels.
- Pigments (cobalt blue, known in ancient times, and Cobalt green).
- Battery sector (e.g. electrodes) estimated as about 11% of production in 2003.
- Steel-belted radial tires.
- Cobalt-60 has multiple uses as a gamma ray source:
 - * It is used in radiotherapy.
 - * It is used in radiation treatment of foods for sterilization (cold pasteurization).
 - * It is used in industrial radiography to detect structural flaws in metal parts.

Cobalt compounds

Oxides

Cobalt oxides

Formula	Colour	Oxidation State	MP	Structure / comments
Co ₂ O ₃		Co ³⁺		
Co ₃ O ₄	black	Co ^{2+/3+}	900-950decomp	normal spinel
CoO	olive green	Co ²⁺	1795	NaCl -antiferromag. < 289 K

Preparations:

Co₂O₃ is formed from oxidation of Co(OH)₂.

CoO when heated at 600-700°C converts to Co₃O₄

Co₃O₄ when heated at 900-950°C reconverts back to CoO.

no stable [Co(H₂O)₆]³⁺ or [Co(OH)₃ exist since these convert to CoO(OH).

[Co(H₂O)₆]²⁺ not acidic and a stable carbonate exists.

Cobalt Blue

One of the earliest uses of Cobalt was in the colouring of glass by the addition of cobalt salts.



The pigment is based on the spinel CoAl₂O₄ and in the laboratory can be readily synthesised by pyrolysis of a mixture of AlCl₃ and CoCl₂.

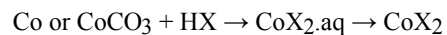
Halides

Cobalt(II) halides

Formula	Colour	MP	μ(BM)	Structure
CoF ₂	pink	1200	-	rutile

CoCl ₂	blue	724	5.47	CdCl₂
CoBr ₂	green	678	-	CdI₂
CoI ₂	blue-black	515	-	CdI₂

Preparations:



Cobalt complexes

The Cobalt(III) ion forms many stable complexes, which being inert, are capable of exhibiting various types of isomerism. The preparation and characterisation of many of these complexes dates back to the pioneering work of [Werner](#) and his students.

Coordination theory was developed on the basis of studies of complexes of the type:

Werner Complexes

[Co(NH ₃) ₆]Cl ₃	yellow
[CoCl(NH ₃) ₅]Cl ₂	red
<i>trans</i> -[CoCl ₂ (NH ₃) ₄]Cl	green
<i>cis</i> -[CoCl ₂ (NH ₃) ₄]Cl	purple

Another important complex in the history of coordination chemistry is [hexol](#). This was the first complex that could be resolved into its optical isomers that did not contain carbon atoms. Since then, only three or four others have been found.

Recently a structure that Werner apparently misassigned has been determined to be related to the original hexol although in this case the complex contains 6 Co atoms, i.e. is hexanuclear. The dark green compound is not resolvable into optical isomers.



Werner's hexol and "2nd hexol"

- Highlight the Co and O sites Highlight the Co and O sites
 Reset the sites Reset the sites

A noticeable difference between chromium(III) and cobalt(III) chemistry is that cobalt complexes are much less susceptible to hydrolysis, though limited hydrolysis, leading to

polynuclear cobaltamines with bridging OH- groups, is well known.

Other commonly occurring bridging groups are NH_2^- , NH^{2-} and NO_2^- , which give rise to complexes such as the bright-blue amide bridged $[(\text{NH}_3)_5\text{Co}-\text{NH}_2-\text{Co}(\text{NH}_3)_5]^{5+}$.

In the preparation of cobalt(III) hexaammine salts by the oxidation in air of cobalt(II) in aqueous ammonia it is possible to isolate blue $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5]^{4+}$. This is moderately stable in concentrated aqueous ammonia and in the solid state but readily decomposes in acid solutions to Co(II) and O_2 , while oxidizing agents such as $(\text{S}_2\text{O}_8)^{2-}$ convert it to the green, paramagnetic $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5]^{5+}$ ($\mu_{300} = 1.7 \text{ B.M.}$).

In the brown compound both cobalt atoms are Co(III) and are joined by a peroxo group, O_2^{2-} , this fits with the observed diamagnetism; in addition the stereochemistry of the central Co-O-O-Co group is similar to that of H_2O_2 .

The green compound is less straightforward. Werner thought that it too involved a peroxo group but in this instance bridging between Co(III) and Co(IV) atoms.

This could account for the paramagnetism, but EPR evidence shows that the 2 cobalt atoms are equivalent, and X-ray evidence shows the central Co-O-O-Co group to be planar with an O-O distance of 131 pm, which is very close to the 128 pm of the superoxide, O_2^- , ion.

A more satisfactory formulation therefore is that of 2 Co(III) atoms joined by a superoxide bridge.

A range of Co(II) dioxygen complexes are known, some of which are able to reversibly bind O_2 from the air. During WWII, some US aircraft carriers are reported to have used these complexes as a solid source for oxy-acetylene welding. By slightly warming the solid complex the oxygen was released and when cooled again oxygen would be coordinated again.

Unlike an oxygen cylinder the solid would not explode if hit by a stray bullet!

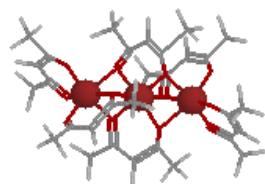
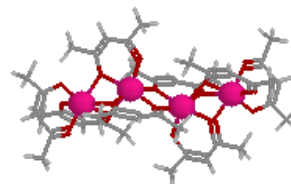


[CosalenO₂]

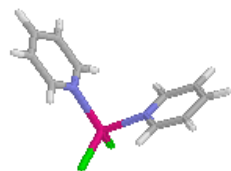
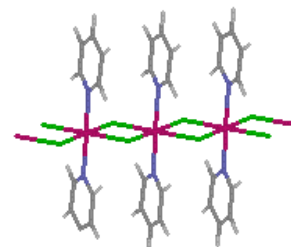
A [laboratory experiment](#) designed to measure the uptake of dioxygen by Cosalen is available online.

$\text{Co}(\text{acac})_3$ is a green octahedral complex of Co(III). In the case of Co(II) a comparison can be made to the Ni(II) complexes.

$\text{Ni}(\text{acac})_2$ is only found to be monomeric at temperatures around 200C in non-coordinating solvents such as n-decane. 6-coordinate monomeric species are formed at room temperature in solvents such as pyridine, but in the solid state $\text{Ni}(\text{acac})_2$ is a trimer, where each Ni atom is 6-coordinate. Note that $\text{Co}(\text{acac})_2$ actually exists as a tetramer.

[Ni(acac)₂]₃[Co(acac)₂]₄

Cobalt(II) halide complexes with pyridine show structural isomerism. Addition of pyridine to cobalt(II) chloride in ethanol can produce blue, purple or pink complexes each having the composition "CoCl₂pyr₂". The structures are 4, 5 and 6 coordinate with either no bridging chlorides or mono- or di- bridged chlorides.

blue-[CoCl₂pyr₂] CN=4pink-[CoCl₂pyr₂] CN=6

See the notes on [isomerism](#) for examples of Co(III) compounds that show linkage and structural isomerism.

Health

see the notes at The University of Bristol on [Vitamin B12 and other Cobalt species essential for good health.](#)

[return to the C21J course outline](#)



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Created and maintained by [Prof. Robert J. Lancashire](#)

*The Department of Chemistry, University of the West Indies,
Mona Campus, Kingston 7, Jamaica.*

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URL <http://wwwchem.uwimona.edu.jm/courses/cobalt.html>