

Chromium Chemistry

History

For the chapter on Chromium chemistry from the Elsevier text "Chemistry of the Elements" by Greenwood and Earnshaw see [On-Line Metals Based Surveys](#). (Note that this link has not worked recently!)

Discovered in 1797 by the French chemist Louis Nicolas Vauquelin, it was named chromium (Greek chroma, "colour") because of the many different colours characteristic of its compounds.

Occurrence

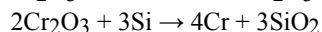
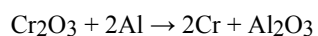
Chromium is the earth's 21st most abundant element (about 122 ppm) and the 6th most abundant transition metal. The principal and commercially viable ore is chromite, FeCr₂O₄, which is found mainly in southern Africa (with 96% of the worlds reserves), the former U.S.S.R and the Philippines. Less common sources include crocoite, PbCrO₄, and chrome ochre, Cr₂O₃, while the gemstones emerald and ruby owe their colours to traces of chromium. See the [International Chromium Development Association web site](#) for more details.

Extraction

Chromite, FeCr₂O₄, is the most commercially useful ore, and is extensively used for extraction of chromium. Chromium is produced in two forms: (Chemistry of the Elements, Greenwood and Earnshaw, Chapter 23).

(a) Ferrochrome by the reduction of chromite with coke in an electric arc furnace. A low-carbon ferrochrome can be produced by using ferrosilicon instead of coke as the reductant. This iron/chromium alloy is used directly as an additive to produce chromium-steels which are "stainless" and hard.

(b) Chromium metal by the reduction of Cr₂O₃. This is obtained by aerial oxidation of chromite in molten alkali to give sodium chromate, Na₂CrO₄, which is leached out with water, precipitated and then reduced to the Cr(III) oxide by carbon. The oxide can be reduced by aluminium (aluminothermic process) or silicon:



The main use of the chromium metal so produced is in the production of nonferrous alloys, the use of pure chromium being limited because of its low ductility at ordinary temperatures. Alternatively, the Cr₂O₃ can be dissolved in sulphuric acid to give the electrolyte used to produce the ubiquitous chromium-plating which is at once both protective and decorative. The sodium chromate produced in the isolation of chromium is itself the basis for the manufacture of all industrially important chromium chemicals. World production of chromite ores approached 12 million tonnes in 1995.

Properties

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



Chromium Compounds

Most compounds of chromium are coloured (why is Cr(CO)₆ white?); the most important are the chromates and dichromates of sodium and potassium and the potassium and ammonium

chrome alums. The dichromates are used as oxidizing agents in quantitative analysis, also in tanning leather. Other compounds are of industrial value; lead chromate is chrome yellow, a valued pigment. Chromium compounds are used in the textile industry as mordants, and by the aircraft and other industries for anodizing aluminium.

Halides

Chromium(III) halides

Formula	Colour	MP	M-X (pm)	μ (BM) ^(b)	Structure
CrF ₃	green	1404	190	-	-
CrCl ₃	red-violet	1152	238	-	CrCl₃
CrBr ₃	green-black	1130	257	-	BiI₃
CrI ₃	black	>500decomp	-	-	-

(b) all 3.7-4.1 BM.

Preparations:

CrX₃ are prepared from Cr with X₂, dehydration of CrCl₃.6H₂O requires SOCl₂ at 650C.

Chromium(II) halides

Formula	Colour	MP	μ (BM)	Structure
CrF ₂	green	894	4.3	distorted rutile
CrCl ₂	white	820-824	5.13	distorted rutile
CrBr ₂	white	844	-	-
CrI ₂	red-brown	868	-	-

Preparations:

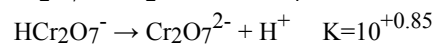
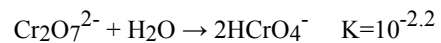
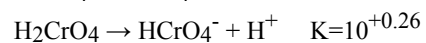
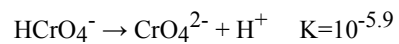
Reduction of CrX₃ with H₂/HX gives CrX₂.

Oxides

Chromium oxides

Formula	Colour	Oxidation State	MP	Magnetic Moment
CrO ₃	deep red	Cr ⁶⁺	197decomp	-
Cr ₃ O ₈	-	intermediate	-	-
Cr ₂ O ₅	-	-	-	-
Cr ₅ O ₁₂ etc	-	-	-	-
CrO ₂	brown-black	Cr ⁴⁺	300decomp	-
Cr ₂ O ₃	green	Cr ³⁺	2437	-antiferromagnetic < 35 C

Dichromate and chromate equilibria is pH dependent:



Hence the variation found for solutions of CrO_3 are:

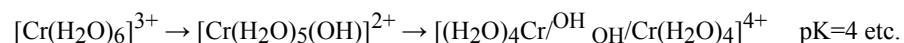
pH > 8 CrO_4^{2-} yellow

pH 2-6 HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ orange-red

pH < 1 $\text{H}_2\text{Cr}_2\text{O}_7$

One of the most obvious characteristics of Cr(III) is that it is acidic i.e it has a tendency to hydrolyse and form polynuclear complexes containing OH bridges in a process known as OLATION.

This is thought to occur by the loss of a proton from coordinated water, followed by coordination of the OH to a second cation:



The ease with which the proton is removed can be judged by the fact that the hexaquo ion ($\text{pK}_a \sim 4$) is almost as strong as acetic acid. Further deprotonation and polymerization can occur and, as the pH is raised, the final product is hydrated chromium(III) oxide or "chromic hydroxide".

Representative Complexes

The Chromium(III) ion forms many stable complexes and since they are inert are capable of exhibiting various types of isomerism.





anhydrous CrCl_3 and hydrated " $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ",

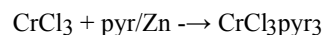
Hydrated chromium chloride, " $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ", exists as hydrate isomers, including:

the violet $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$

the dark green *trans*- $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ salt shown above, etc.

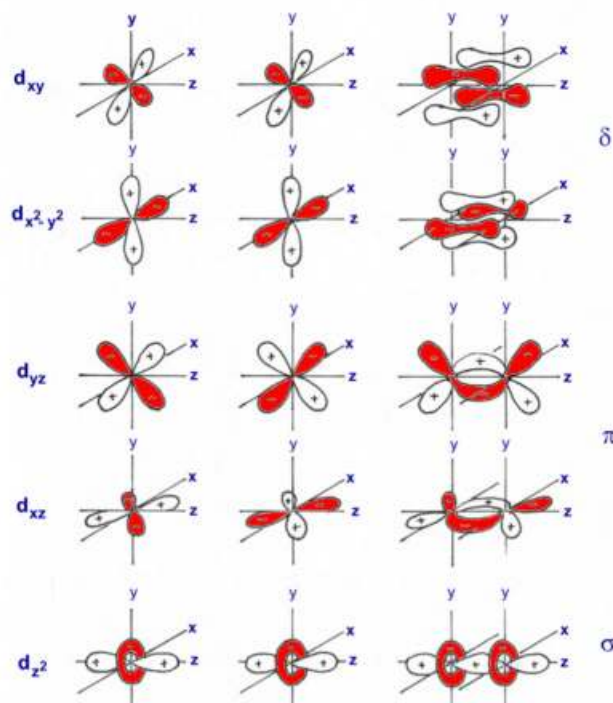
the pale green $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$

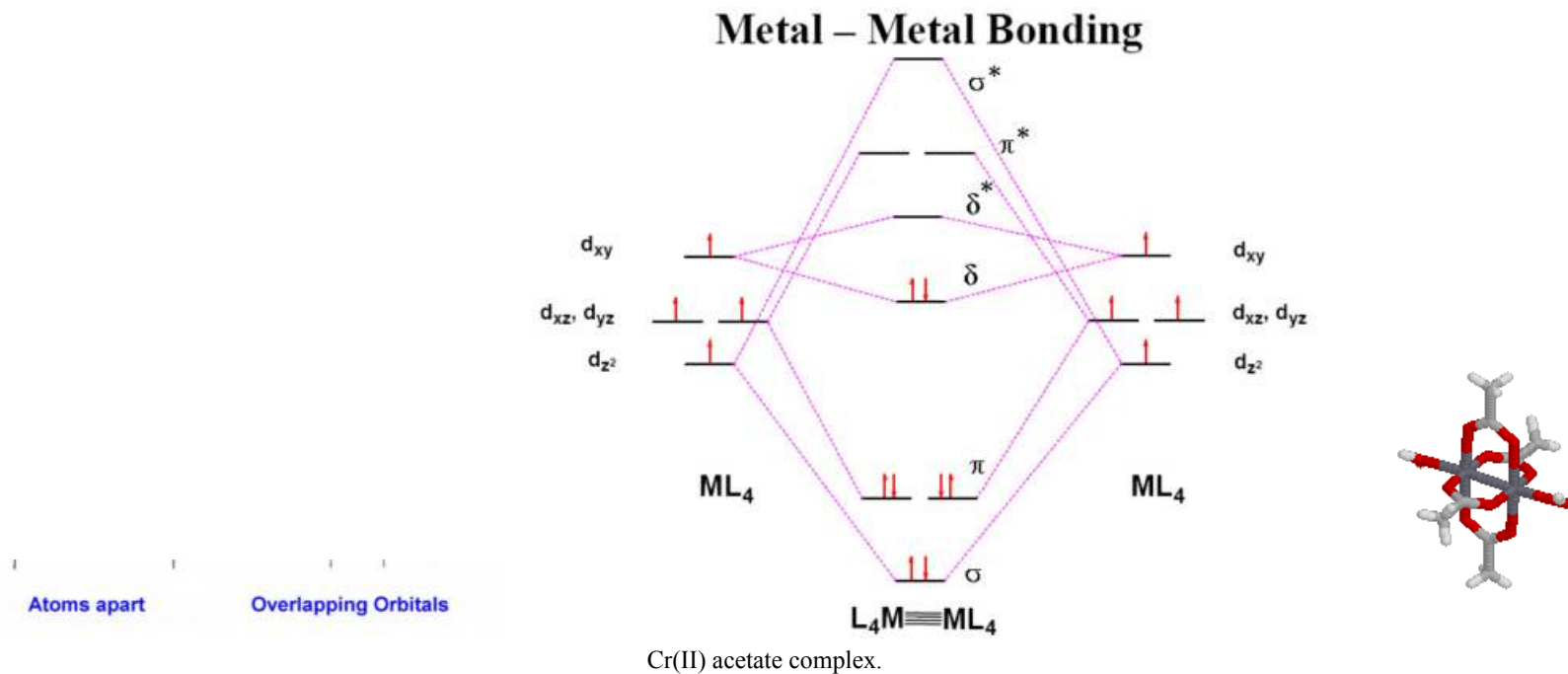
Anhydrous CrCl_3 reacts with pyridine only in the presence of Zinc powder. This allows a small amount of the Cr(II) ion to be formed, which is very labile but unstable with respect to oxidation back to Cr(III).



See the [laboratory manual for this course](#) for a range of other Cr(III) complexes for which you should know the structure.

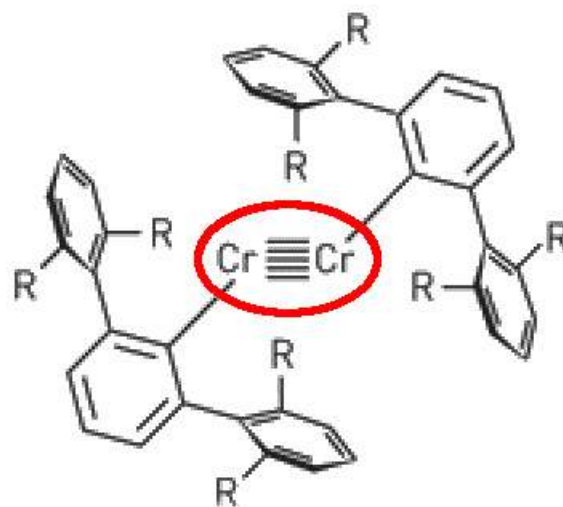
$[\text{Cr}_2(\text{OAc})_4] \cdot 2\text{H}_2\text{O}$ is an example of a Cr(II) complex which is reasonably stable in air once isolated. Each Cr(II) ion has 4 d electrons but the complex is found to be diamagnetic which is explained by the formation of a quadruple bond between the two metal ions. The Cr-Cr bond distance in a range of these quadruply bonded species has been found to vary between 195-255 pm.





In case you think that quadruple bonds are as far as it goes....

A recent report describes the structure of a Cr complex with a quintuple bond between two Cr(I) ions.



Cr(I) - Cr(I) quintuple bonded structure.

The compound $Ar'CrCrAr'$ ($R = \text{isopropyl}$) was very air and moisture sensitive and crystallised as dark red crystals. X-ray diffraction revealed a Cr-Cr bond length of about 1.84

angstroms and a planar, trans-bent core geometry. Published in Science online by P Power et. al., UCLA Davis, 22 September 2005 [DOI: 10.1126/science.1116789].

Uses

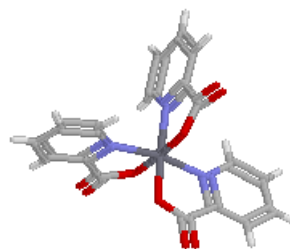
More than half the production of chromium goes into metallic products, and about another third is used in refractories. It is an ingredient in several important catalysts. The chief use of chromium is to form alloys with iron, nickel, or cobalt. The addition of chromium imparts hardness, strength, and corrosion resistance to the alloy. In the stainless steels, chromium makes up 10 percent or more of the final composition. Because of its hardness, an alloy of chromium, cobalt, and tungsten is used for high-speed metal-cutting tools. When deposited electrolytically, chromium provides a hard, corrosion-resistant, lustrous finish. For this reason it is widely used as body trim on automobiles and other vehicles. The extensive use of chromite as a refractory is based on its high melting point, its moderate thermal expansion, and the stability of its crystalline structure.

In chromites and chromic salts, chromium has a valence of +3. Most of these compounds are green, but some are red or blue. Chromic oxide (Cr_2O_3) is a green solid. In chromates and dichromates, chromium has a valence of +6. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is a red, water-soluble solid that, mixed with gelatin, gives a light-sensitive surface useful in photographic processes. The chromates are generally yellow, the best known being lead chromate (PbCrO_4), an insoluble solid widely used as a pigment called chrome yellow. Chrome green is a mixture of chrome yellow and Prussian blue.

Chromium is used to harden steel, to manufacture stainless steel, and to form many useful alloys. Much is used in plating to produce a hard, beautiful surface and to prevent corrosion. Chromium gives glass an emerald green colour and is widely used as a catalyst. The refractory industry has found chromite useful for forming bricks and shapes, as it has a high melting point, moderate thermal expansion, and stability of crystalline structure.

Health

Chromium is an essential trace element in mammalian metabolism. In addition to insulin, it is responsible for reducing blood glucose levels, and is used to control certain cases of diabetes. It has also been found to reduce blood cholesterol levels by diminishing the concentration of (bad) low density lipoproteins "LDLs" in the blood. It is supplied in a variety of foods such as Brewer's yeast, liver, cheese, whole grain breads and cereals, and broccoli. It is claimed to aid in muscle development, and as such dietary supplements containing chromium picolinate (its most soluble form), is very popular with body builders.



mer- isomer of Cr(III) picolinate complex.

Ammonium Reineckate, $\text{NH}_4(\text{Cr}(\text{NH}_3)_2(\text{SCN})_4) \cdot \text{H}_2\text{O}$, is used to test for the presence of dihydromorphinone and other substances generally found in persons involved in substance abuse.

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