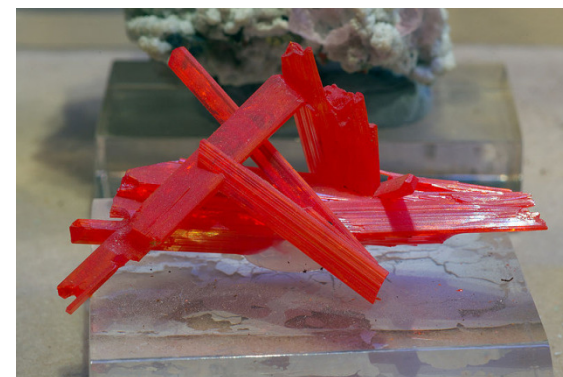


Chromium Chemistry



Elemental Chromium

- Chief ore is chromite (FeCr_2O_4), which has a spinel structure consisting of Fe(II) [T_d] and Cr(III) [O_h].
- Pure Cr is a white, hard, lustrous, and brittle metal.
- First discovered in 1797 in the mineral crocoite (*lead chromate*) which is famous for its deep yellow color and is used extensively in paints.
- ***The name chromium is derived from the Greek word "chrōma", meaning color, because many of its compounds are intensely colored.***
- Extremely resistant to corrosive reagents, which accounts for its extensive use as an electroplated protective coating.
- Readily dissolves in mineral acids (HCl , H_2SO_4) but not oxidizing acids (HNO_3)

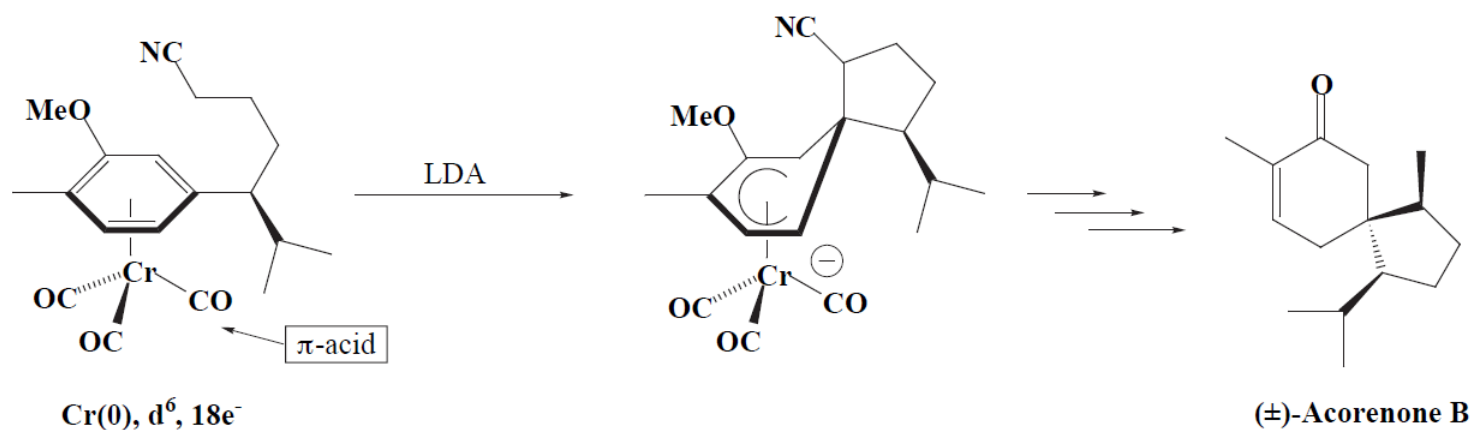
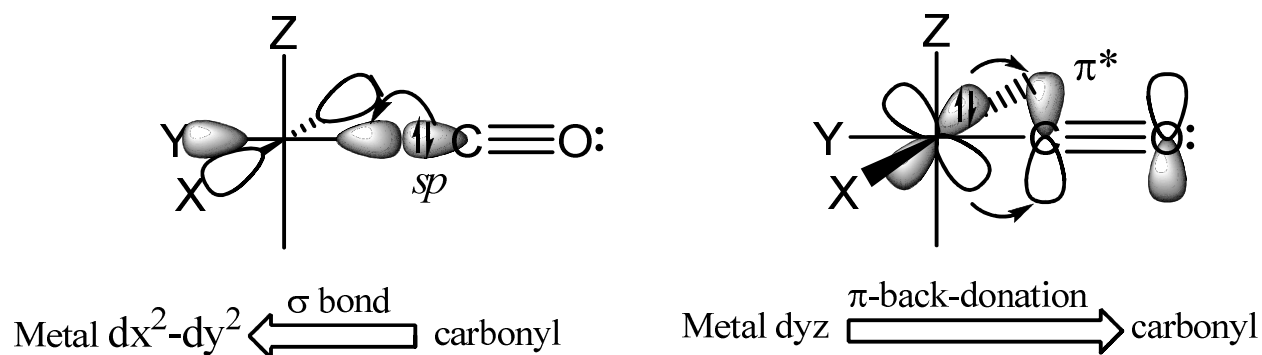
Chromium Oxidation States

- Oxidation states range from +2 to +6
- The highest oxidation state Cr(VI) exists only in oxo forms (strongly oxidizing)
- In today's lab we will see +6, +3, and +2

| <i>Oxidation state</i> | +6 | +3 | +2 |
|-------------------------------|--|--------------|--------------|
| <i>Ions</i> | $\text{CrO}_4^{2-} / \text{Cr}_2\text{O}_7^{2-}$ | Cr(III) (aq) | Cr(II) (aq) |
| <i>Color</i> | orange/red-orange | green | blue-violet |
| <i>Configuration</i> | $3d^0$ | $3d^3$ | $3d^4$ |
| <i>Magnetism</i> | diamagnetic | paramagnetic | paramagnetic |

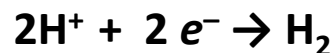
Cr(0)

- This low valent oxidation state of Cr can be stabilized by a highly electron withdrawing ligand-set by back-donation into a ligand π^* -orbital.



Cr(II)

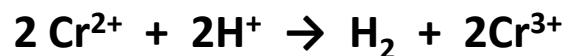
- The most stable and generally most important oxidation states of chromium are Cr(II) and Cr(III).
- Cr(III) is typically green, and Cr(II) is usually blue-violet. Cr³⁺ ion has the configuration 3d³, and Cr²⁺ ion has the configuration 3d⁴, so both species are expected to be paramagnetic in an O_h environment.
- [Cr^{II}(OH₂)₆]²⁺ is prepared by the dissolution of elemental Cr in mineral acid resulting in a bright blue solution.
- Alternatively, [Cr^{II}(OH₂)₆]²⁺ can be prepared by the reduction of Cr(III) by electrochemical or chemical (Zn/Hg) methods in the absence of O₂.
- Even in the absence of O₂ [Cr^{II}(OH₂)₆]²⁺ will oxidize with concurrent H₂ evolution, i.e. H⁺ reduction.



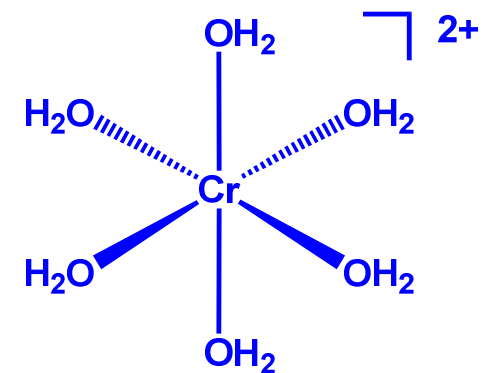
$$E^0 = 0.000 \text{ V}$$



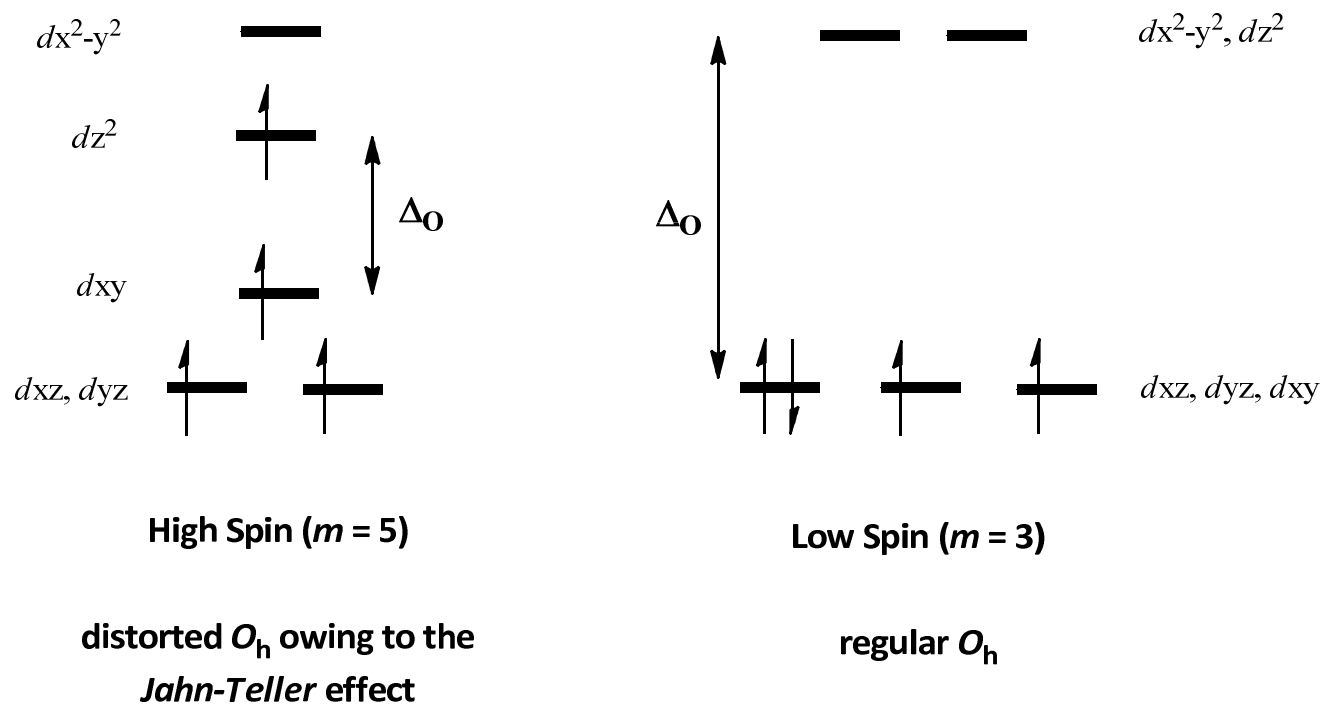
$$E^0 = -0.410 \text{ V}$$



$$E_{\text{cell}} = +0.410 \text{ V}$$

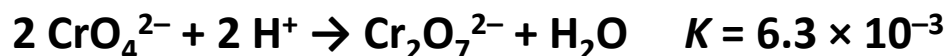
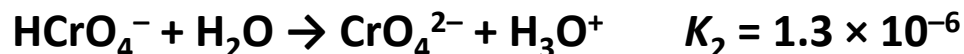


- O_h Cr(II) complexes can exist in either high- or low-spin configurations depending upon the O_h ligand-set involved.



Potassium Dichromate - Cr(VI)

- Potassium dichromate, $K_2Cr_2O_7$, is the starting material for today's synthesis.
- In basic solution, chromium(VI) exists as the orange-colored tetrahedral CrO_4^{2-} ion.
- In acid solution, this can become $HCrO_4^-$ but dimerization to red-orange $Cr_2O_7^{2-}$ predominates:

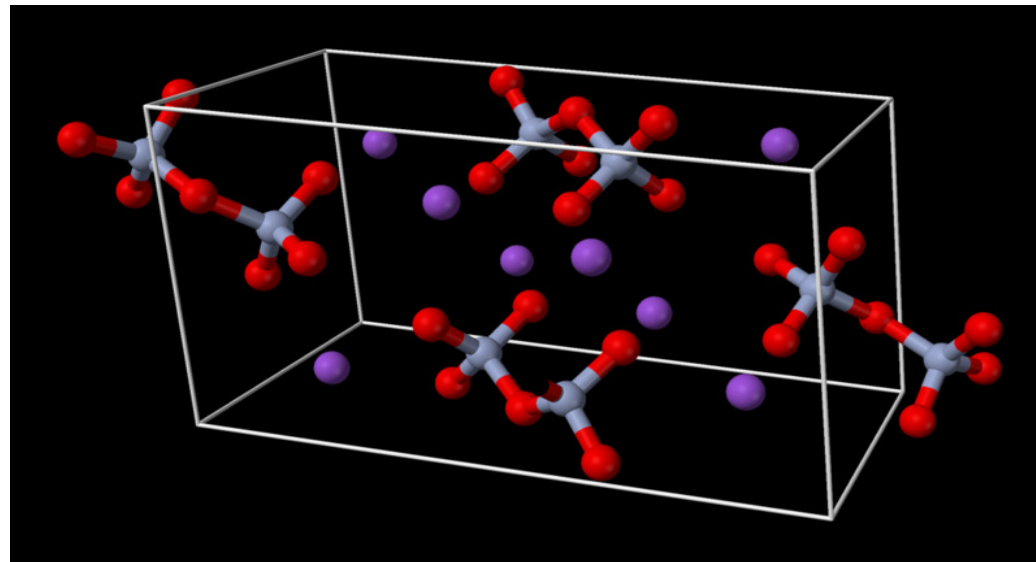
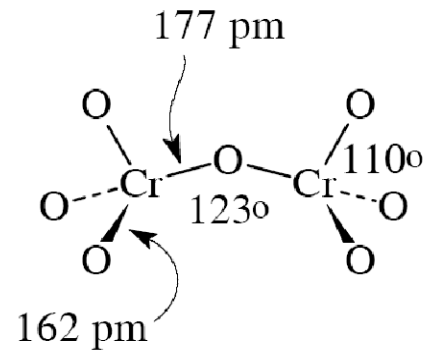


CARCINOGEN



- The configuration of Cr in both chromate and dichromate ions is d^0 [Cr(VI)]. The intense colors of CrO_4^{2-} and $Cr_2O_7^{2-}$ are the result of **ligand-to-metal (O→Cr) charge transfer bands**.
- Chromic acid in aqueous sulfuric acid and acetone is known as the Jones reagent, which will oxidize 1^0 and 2^0 alcohols to carboxylic acids and ketones respectively, while rarely affecting unsaturated bonds.

- The dichromate ion has two tetrahedrally coordinated Cr atoms linked by an oxygen bridge:



Redox Synthesis

- In this synthesis we will reduce Cr(VI) to Cr(III) and then to Cr(II).
- *Dichromate is a strong oxidizing agent:*



- Cr(III) is a weak oxidizing agent, which requires a strong reducing agent to produce Cr(II):



- In this synthesis, zinc metal serves as the strong reducing agent:

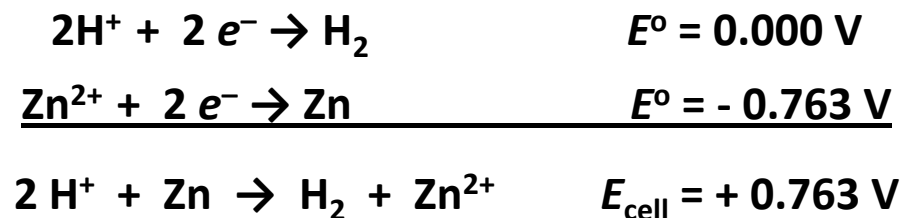


Overall Redox Reaction Uncertain

- From the electrode potentials, it might be assumed that the reduction of Cr(VI) to Cr(II) is accomplished by Zn as the reducing agent, in which case the balanced equation would be



- But in this preparation, Zn and H^+ from the acid are also reacting to produce $\text{H}_2(g)$:



(vigorous reaction $\Delta G^\circ = -147 \text{ kJ mol}^{-1}$)

- ***Hydrogen gas might be the reducing agent for converting Cr(VI) to Cr(III).***
- If so, the reduction of Cr(III) to Cr(II) would then be effected by Zn as the reducing agent in a second step.



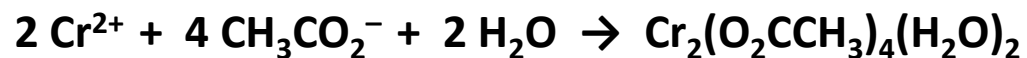
- More likely, the production of Cr²⁺ is a mixture of reduction by H₂ and reduction by Zn.

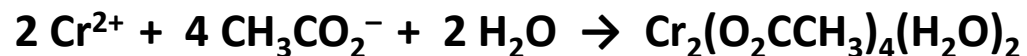


- Regardless of the exact stoichiometry, the limiting reagent is Cr₂O₇²⁻, from which twice as many moles of Cr²⁺ is produced.

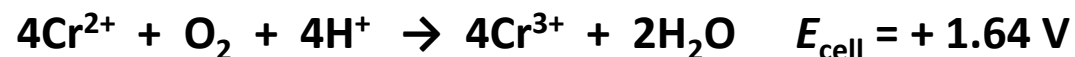
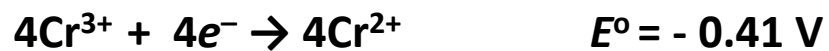
Reaction Summary

- *Color of the original dichromate solution changes from red/orange to green and then to blue.*
- *When the solution is blue, conversion to Cr²⁺ is complete.*
- At this point, using the pressure from the evolving H₂(g), the solution is pumped into a solution of sodium acetate, where the complex forms and is precipitated as a brick-red solid:





- When wet, the complex is subject to oxidation to Cr(III) from oxygen:

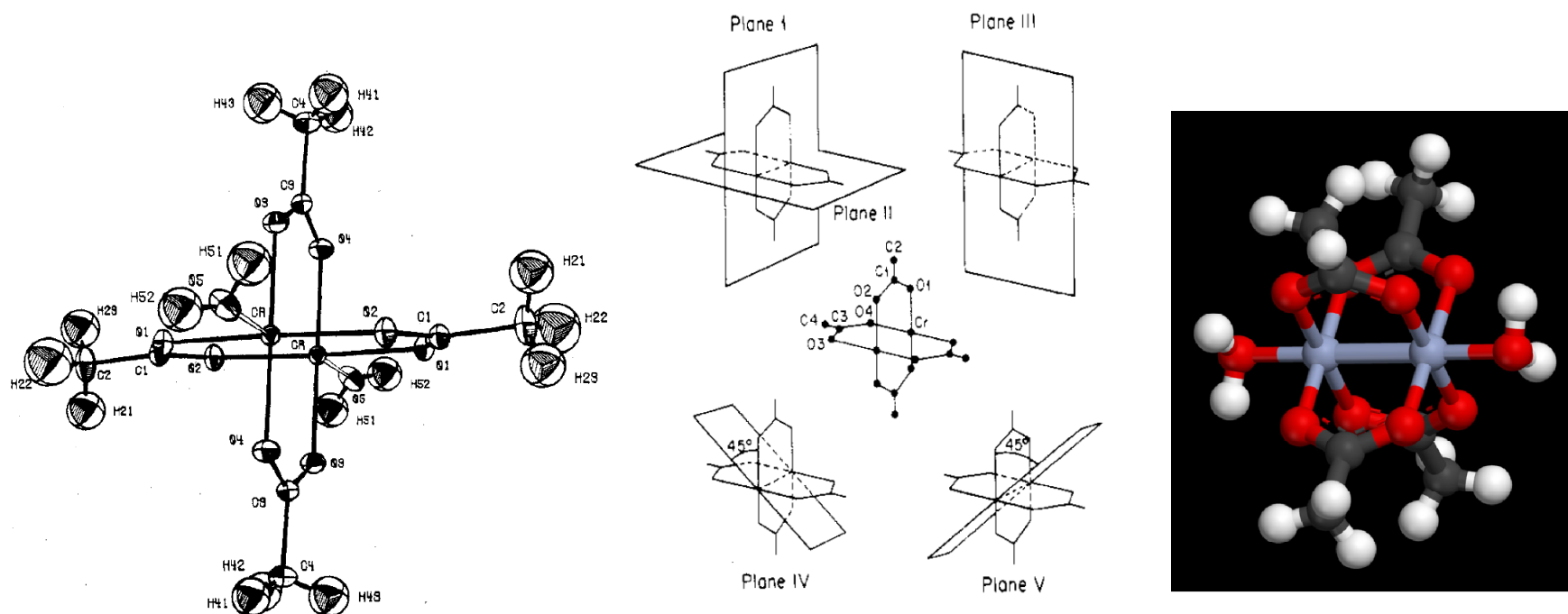


***Avoid sucking air through the wet product
during the cold water and alcohol washes.***

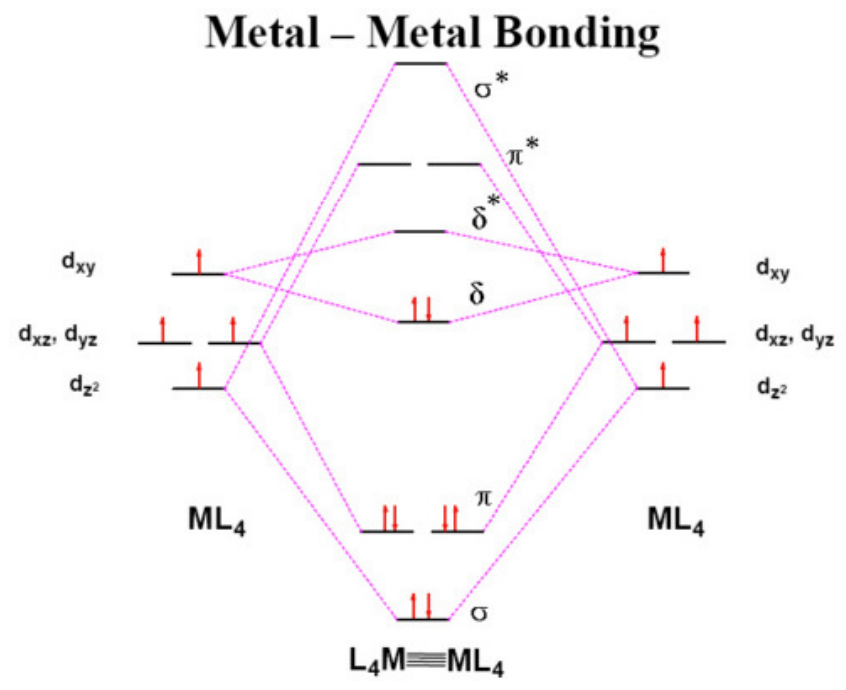
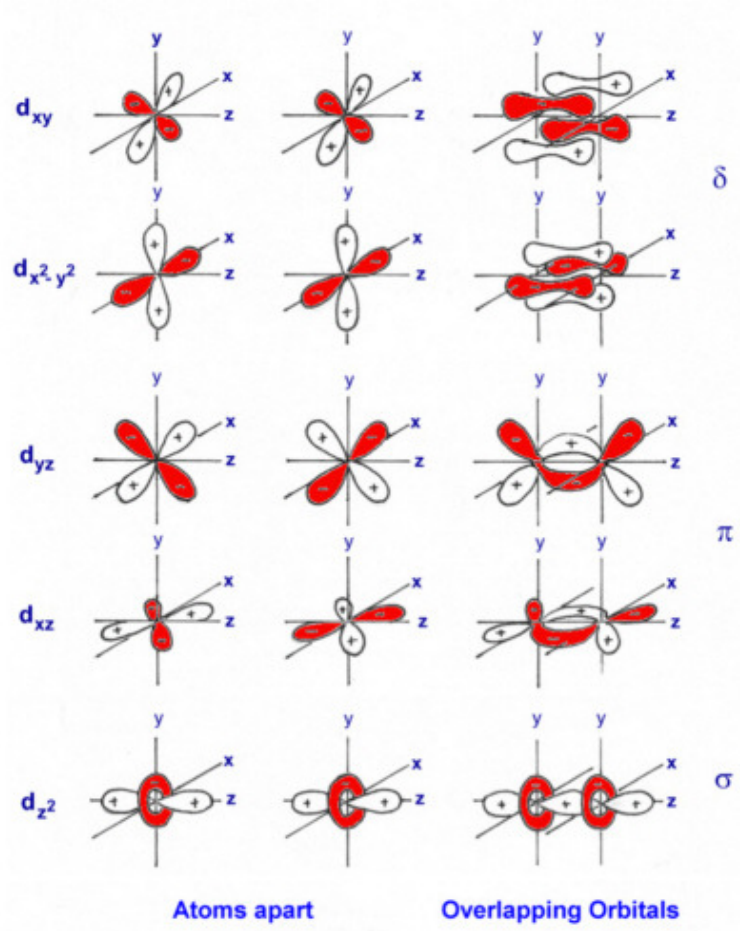
- After the final ether wash, allow air to pass through the product on the filter for about 30 sec., then collect it on a large piece of dry filter paper or a porcelain plate to allow the residual ether to evaporate.

Chromium(II) Acetate

- Chromium(II) acetate dihydrate, $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$, was discovered in 1844.
- It has long been regarded as unusual for a Cr(II) compound because it is brick-red and diamagnetic.
- It is the longest-known example of a family of compounds that have the general formula $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$, which have the following structure:



- 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 1.95-2.55 Å.



Cr(I)

- In the absence of π -back-donation low valent oxidation states of Cr such as Cr(I) can be stabilized by strong σ -donor ligands, i.e. strong field ligands:

