Chromium(III) Chloride

$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

anhydrous $\text{CrCl}_3$
Obtaining Non-hydrated Metal Halides

- Many ionic metal halides and other ionic salts are hydrated with a specific number of water molecules per formula unit.
- *Water molecules may occupy specific sites within the crystal lattice or may be directly coordinated to the cation.*

\[
\begin{align*}
\text{CaCl}_2\cdot2\text{H}_2\text{O} & \quad \text{lattice } \text{H}_2\text{O} \\
\text{BeCl}_2\cdot4\text{H}_2\text{O} & \quad \text{coordinated } \text{H}_2\text{O} \\
\text{CrCl}_3\cdot6\text{H}_2\text{O} & \quad \text{coordinated } \text{H}_2\text{O} \\
\text{CuSO}_4\cdot5\text{H}_2\text{O} & \quad \text{lattice } \text{H}_2\text{O} + \text{coordinated } \text{H}_2\text{O}
\end{align*}
\]

- Salts with lattice waters of hydration can often be dehydrated by simply heating or heating in vacuum.

\[
\text{CaCl}_2\cdot2\text{H}_2\text{O} + \Delta \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}
\]
• *Salts with coordinated water usually decompose to a mixture of oxides or oxohalides, often with no specific stoichiometry.*

• Sometimes anhydrous halides can be formed from the hydrated salts by *chemically destroying the water of hydration with a reagent such as thionyl chloride.*

\[
[\text{Cr(H}_2\text{O)}_6]\text{Cl}_3 + 6\text{SOCl}_2 + \Delta \rightarrow \text{CrCl}_3 + 12 \text{HCl} + 6\text{SO}_2
\]

• An alternative approach is to use either the metal or metal oxide and a halogenating agent at high temperature; e.g.,

\[
\text{Cr}_2\text{O}_3 + 3\text{CCl}_4 + \Delta \rightarrow 2\text{CrCl}_3 + 3\text{COCl}_2
\]

• This is the method used in today’s synthesis.
• **CrCl$_3$ is not ionic**, but rather has a network solid structure with bridged Cl$^-$ ions and octahedrally coordinated Cr(III) ions, which form layers.

• Although CrCl$_3$·6H$_2$O is green, solid CrCl$_3$ is purple.

• *The solid consists of shiny flakes, owing to its layered structure.*

• The stability of the network structure makes CrCl$_3$ **insoluble in water** and most other solvents.
Notes on Synthesis

- The reaction is carried out at 700 °C in a Vycor (quartz) tube in a tube furnace.
- Nitrogen is bubbled through liquid CCl₄, and the stream of N₂/CCl₄ is passed over a pile of green Cr₂O₃ in the center of the tube.
- As CrCl₃ is formed it sublimes and is carried in the nitrogen stream to the cooler far end of the tube, where it condenses.
- A byproduct of the reaction is **poisonous phosgene gas**, COCl₂.

\[
\text{Cr}_2\text{O}_3 + 3\text{CCl}_4 \quad \Delta \quad 2\text{CrCl}_3 + 3\text{COCl}_2
\]

- Be sure the fume hood is working properly!
• Adjusting the \( \text{N}_2(g) \) flow rate and maintaining a consistent flow of \( \text{CCl}_4 \) is critical to successful synthesis.

• Too slow a rate will cause the reaction to take excessively long time.

• Too fast a rate causes product to be blown out the end of the tube without condensing. (Watch for wisps of white smoke.)

• The reaction proceeds until nearly all of the \( \text{Cr}_2\text{O}_3 \) in the center of the tube is gone, about 3 hours.

• If available, product from previous years will be provided for you to carry out the confirming tests, rather than waiting for your own product.