Chromium(III) Chloride

$CrCl_3 \cdot 6H_2O$

anhydrous $CrCl_3$

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.***

$CaCl_2 \cdot 2H_2O$	lattice H_2O
$BeCl_2 \cdot 4H_2O$	coordinated H_2O
$CrCl_3 \cdot 6H_2O$	coordinated H_2O
$CuSO_4 \cdot 5H_2O$	lattice H_2O + coordinated H_2O

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

$$CaCl_2 \cdot 2H_2O + \Delta \rightarrow CaCl_2 + 2H_2O$$

- ***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.***

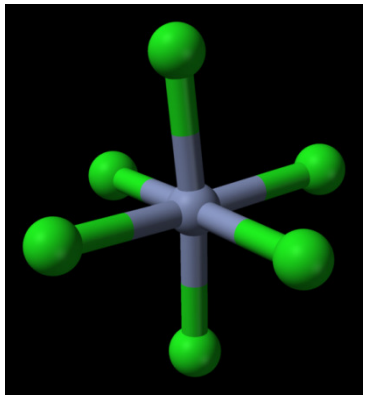
$$[Cr(H_2O)_6]Cl_3 + 6SOCl_2 + \Delta \rightarrow CrCl_3 + 12\ HCl + 6SO_2$$

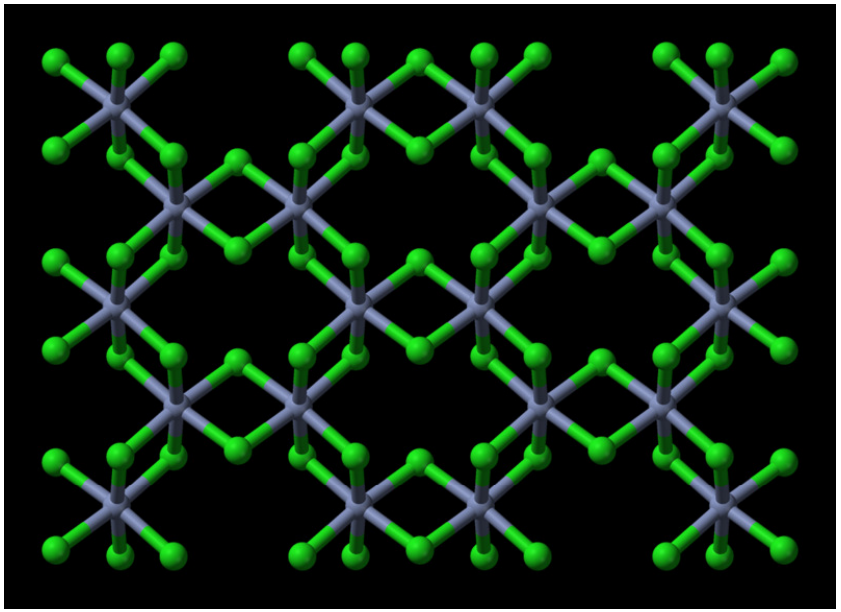
- An alternative approach is to use either the metal or metal oxide and a halogenating agent at high temperature; e.g.,

$$Cr_2O_3 + 3CCl_4 + \Delta \rightarrow 2CrCl_3 + 3COCl_2$$

- This is the method used in today's synthesis.

Structure of $CrCl_3$





- ***$CrCl_3$ is not ionic***, but rather has a network solid structure with bridged Cl^- ions and octahedrally coordinated Cr(III) ions, which form layers.
- Although $CrCl_3 \cdot 6H_2O$ 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 CCl_4, and the stream of N_2/CCl_4 is passed over a pile of green Cr_2O_3 in the center of the tube.
- As $CrCl_3$ is formed it sublimes and is carried in the nitrogen stream to the cooler far end of the tube, where it condenses.
- A by product of the reaction is **poisonous phosgene gas**, $COCl_2$.

$$Cr_2O_3 + 3CCl_4 + \Delta \rightarrow 2CrCl_3 + 3COCl_2$$

- Be sure the fume hood is working properly!

- Adjusting the N_2(*g) flow rate and maintaining a consistent flow of* 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 Cr_2O_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.