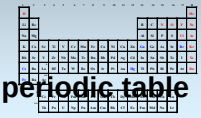
Chromium

A case study



- **Element no. 24 of the periodic table**
- **Atomic symbol *Cr***
- **"Chromium" from "colour"** κρωμα: skin, colour
- **d-block metal**
- **Many co-ordination compounds**
  Appears most often as Cr(III) $[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$

Chromium ore

Chromite ($FeCr_2O_4$)
- large deposits in South Africa

Isolation of chromium metal

- $FeCr_2O_4 + NaOH + O_2 \rightarrow Na_2CrO_4 + Fe_2O_3 + H_2O$
- $Na_2CrO_4(aq) + C \rightarrow Cr_2O_3 + Na_2CO_3(aq)$
- $Cr_2O_3 + Al \rightarrow Cr + Al_2O_3$

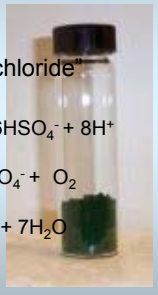
Chromium nuggets

- Hard, gray metal
- Density 7.2 $g{\cdot}ml^{-1}$
- Melting point 1890 ^oC
- Corrosion resistant

Metal + acid

- $Cr + 2H^+ \rightarrow Cr_{aq}^{2+} + H_2(g)$ $E^o(Cr^{2+}/Cr) = -0.91V$
  light blue solution in hydrochloric acid
- $2Cr_{aq}^{2+} + 2H^+ \rightarrow 2Cr_{aq}^{3+} + H_2(g)$ $E^o(Cr^{3+}/Cr^{2+}) = -0.41V$
  green solution in hydrochloric acid

$[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$



Composition of "green chromium(III) chloride"

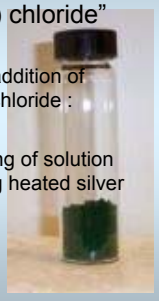
1. Chromium analysis

- $2Cr_{aq}^{3+} + 3S_2O_8^{2-} + 7H_2O \rightarrow Cr_2O_7^{2-} + 6HSO_4^- + 8H^+$
- Excess $2S_2O_8^{2-} + 2H_2O$ heated $\rightarrow 4HSO_4^- + O_2$
- $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$
  Excess Fe^{2+} determined by $Cr_2O_7^{2-}$

$[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$

Composition of ”green chromium(III) chloride”

2. Chloride analysis
   a. Dissolution of solid in nitric acid and addition of silver nitrate; weighing heated silver chloride :
      $M_1 = m_1/n_1$
   b. Dissolution of solid in nitric acid, boiling of solution and addition of silver nitrate; weighing heated silver chloride
      $M_2 = m_2/n_2$
      $M_1 = 3\ M_2$



$[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$

Stabilty

$Cr(H_2O)_6^{3+} + nCl^- \rightarrow Cr(H_2O)_{6-n}Cl^{(3-n)+}$

$\log K_1 = -1.2$, $\log\beta_2 = -3.3$

Kinetics slow

$Cr(H_2O)_6^{3+} + H_2O^* \rightarrow Cr(H_2O)_5H_2O^{*3+} + H_2O$

$k = \sim 10^{-5}\ sec^{-1}$

Synthesis of new compound

from green chromium(III) chloride

- green solution in DMSO
- destillation of water + DMSO azeotropic mixture
- to give a violet solution of $[CrCl_3(DMSO)_3]$
- added to an excess liquid 1,2-ethanediamine gives an brown mass
- mixture dissolves in dilute hydrochloric acid with a yellowish brown colour

New yellow compond

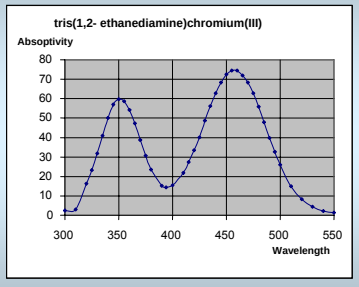
- Recrystallised from dilute HCl
  (separation by filtration)

1,2-ethanediamine abbreviated as ”en”

$[Cren_3]Cl_3{\cdot}3H_2O$

- **Light sensitive**
- **Soluble in water**

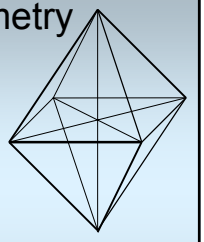
Absorption spectrum



$(\lambda, \varepsilon)_{max}$ = (457 , 75.0), (351 , 60.5) og $(\lambda, \varepsilon)_{min}$ = (394 , 14.5).

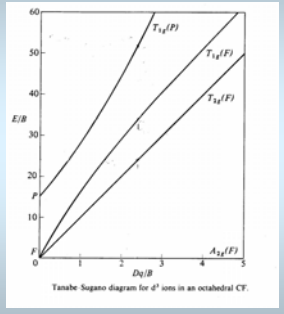
Octahedral Geometry

A regular octahedron with



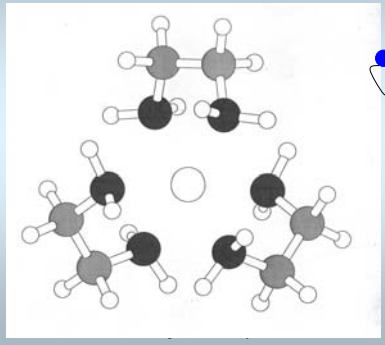
- Cr(III) ion (the central atom) in the centre and
- Three 1,2-ethanediamines as bidentate ligands
- 6 N-atoms in the 6 corners of the octahedron in the same distance from the centre

Ligand field model

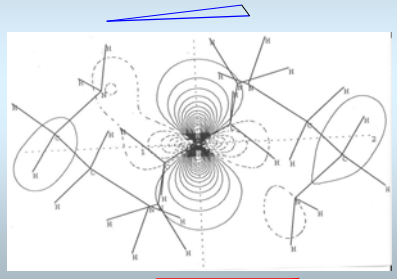


- $\nu_1(^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$= 21600 cm-1
- $\nu_1(^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$= 28500 cm-1
- Δ=10Dq = 21600 cm^{-1}
- B = 650 cm^{-1}

Symmetry



Quantum chemical calculation



Thermodynamics

- Equilibrium:

$[Cr(H_2O)_6]^{3+} + 3en \Leftrightarrow [Cren_3]^{3+} + 6H_2O$

$$\beta_3 = \frac{[Cren_3^{3+}]}{[Cr(H_2O)_6^{3+}]\cdot[en]^3}$$

$\log\beta_3$= 19.4 (24 °C; 1.00M NaCl) ; logK = 6.43

Other properties

- Magnetic behaviour
- Crystal form
- Distances and angles between atoms
- IR spectrum
- Reactivity
- Redox behaviour
- and so on……..

Dimensions in Chemistry

LANGUAGE	⟷	MATTER
THEORY	⟷	OBSERVATION
MODEL	⟷	EXPERIMENT
THERMODYNAMICS	⟷	QUANTUM CHEMISTRY
STRUCTURE	⟷	FUNCTION
LAB WORK	⟷	CALCULATION
SAFETY	⟷	INVESTIGATION
PREPARATION	⟷	CHARACTERISATION
SEPARATION	⟷	MIXING
SYNTHESIS	⟷	ANALYSIS
QUANTITATIVE	⟷	QUALITATIVE
PURE	⟷	APPLIED