

Chromium

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Chromium





A case study

- Element no. 24 of the **periodic table**
- Atomic symbol **Cr**
- "Chromium" from "colour" красота: skin, colour
- d-block metal
- Appears most often as **Cr(III)** $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$
- Many co-ordination compounds

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Electrolytic chromium-plating

In acidic chromate(VI)-baths chromium metal is deposited on the cathode

$$\text{CrO}_3 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Cr} + 3\text{H}_2\text{O}$$

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Chromium ore



Chromite (FeCr_2O_4)
- large deposits in South Africa

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Isolation of chromium metal

- $\text{FeCr}_2\text{O}_4 + \text{NaOH} + \text{O}_2 \rightarrow \text{Na}_2\text{CrO}_4 + \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$
- $\text{Na}_2\text{CrO}_4(\text{aq}) + \text{C} \rightarrow \text{Cr}_2\text{O}_3 + \text{Na}_2\text{CO}_3(\text{aq})$
- $\text{Cr}_2\text{O}_3 + \text{Al} \rightarrow \text{Cr} + \text{Al}_2\text{O}_3$

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Chromium nuggets

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

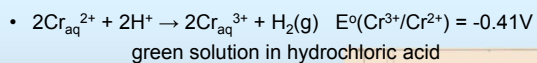
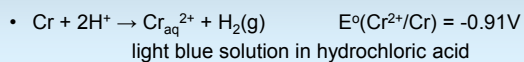


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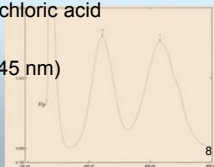
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Metal + acid



green solution: ($\lambda_{\text{max}} = 635 \text{ nm} ; 445 \text{ nm}$)



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$[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$

Composition of "green chromium(III) chloride"
 $\text{CrCl}_3(\text{H}_2\text{O})_6$

1. Chromium analysis

- $2\text{Cr}_{\text{aq}}^{3+} + 3\text{S}_2\text{O}_8^{2-} + 7\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 6\text{HSO}_4^- + 8\text{H}^+$
- Excess $2\text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O}$ heated $\rightarrow 4\text{HSO}_4^- + \text{O}_2$
- $\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$
Excess Fe^{2+} determined by standard $\text{Cr}_2\text{O}_7^{2-}$



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Safety: Hazard symbols for $\text{K}_2\text{Cr}_2\text{O}_7$

New symbols in EU since 2010

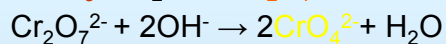
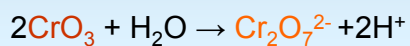
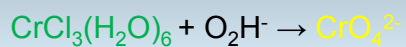


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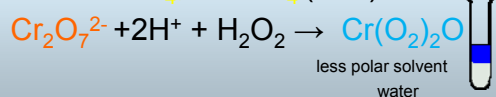
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Cr(IV)



PbCrO₄, BaCrO₄ (Hac)

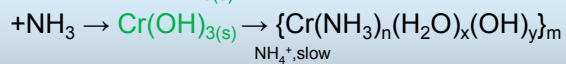
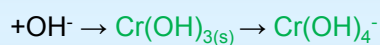
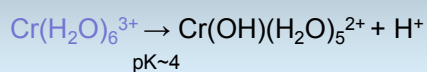


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Cr(H₂O)₆³⁺



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[CrCl₂(H₂O)₄]Cl·2H₂O

Composition of
"green chromium(III) chloride"

2. Chloride analysis

- a. Dissolve solid in nitric acid and add silver nitrate; weigh dry silver chloride :

$$M_1 = m_1/n_1$$

- b. Dissolve solid in nitric acid, boil the solution and add silver nitrate; weigh dry silver chloride

$$M_2 = m_2/n_2$$

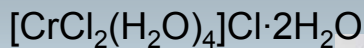
$$M_1 = 3 M_2$$



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Composition of "green chromium(III) chloride"

3. Thermogravimetric analysis

Loss of mass at $t > 100\text{ }^\circ\text{C}$

Water: $n(\text{H}_2\text{O})/n(\text{Cr}) = 2.0$

Stoichiometry: $\text{CrCl}^a_2\text{Cl}^b(\text{H}_2\text{O}^a)_4(\text{H}_2\text{O}^b)_2$

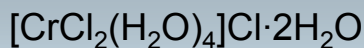
4 water molecules and 2 Cl^- make stronger bonds to Cr^{3+} than 1 Cl^- and 2 water molecules



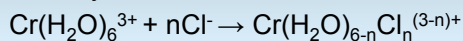
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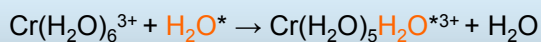
Stability



$$\log K_1 = -1.20, \log \beta_2 = -3.27, \log \beta_3 = -6.43$$

$$(\log K_2 = -2.07, \log K_3 = -3.16)$$

Kinetics slow

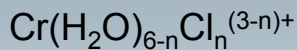


$$k = \sim 10^{-5} \text{ sec}^{-1}$$

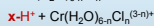
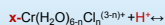
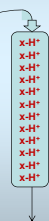
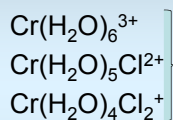
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heat solution \rightarrow approach equilibrium



$$K_n < K_{n+1}$$

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$\text{Cr}(\text{H}_2\text{O})_6^{3+}$

Violet ($\lambda_{\text{max}} = 575, 409, 261 \text{ nm}$)
in crystals and in solution

as nitrate



or



perchlorate

^4P — $^4\text{T}_1$
 ^4F — $^4\text{T}_1$
 — $^4\text{T}_2$
 — $^4\text{A}_2$

low intensity ($\epsilon \sim 15 \text{ (M}\cdot\text{l)}^{-1}$)

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Synthesis of new compound

from green chromium(III) chloride

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

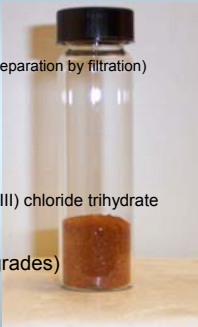
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New yellow compound

- Recrystallised from dilute HCl (separation by filtration)

1,2-ethanediamine abbreviated as "en"

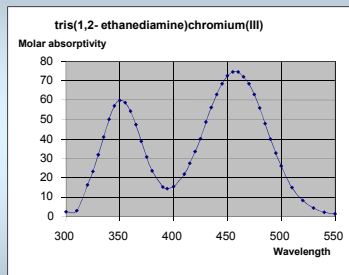
- Formula: $[\text{Cren}_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$
- Name: tris(1,2-ethanediamine)chromium(III) chloride trihydrate
- Two properties
 - **Light sensitive** (darkens and degrades)
 - **Soluble in water**



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Absorption spectrum

aqueous solution



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

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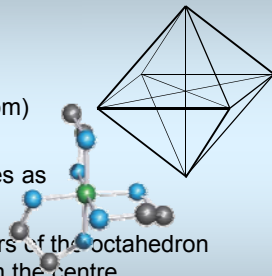
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Octahedral Geometry

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 with equal distances from the centre

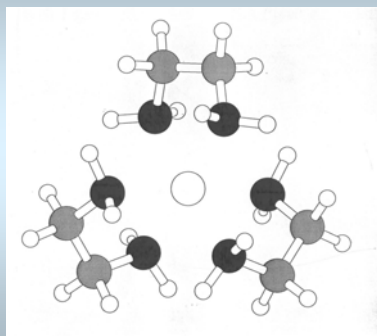


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Symmetry



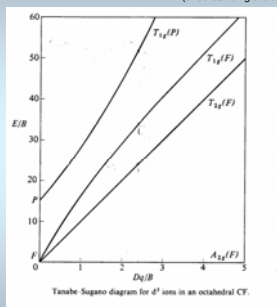
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Ligand field model

(understanding of absorption spectrum)



- $\nu_1(^4A_{2g}(F) \rightarrow ^4T_{2g}(F)) = 21600 \text{ cm}^{-1}$
- $\nu_2(^4A_{2g}(F) \rightarrow ^4T_{1g}(F)) = 28500 \text{ cm}^{-1}$
- $\Delta = 10Dq = 21600 \text{ cm}^{-1}$
- $B = 650 \text{ cm}^{-1}$

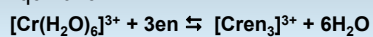
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Thermodynamics

- Equilibrium:



$$\beta_3 = \frac{[\text{Cren}_3^{3+}]}{[\text{Cr}(\text{H}_2\text{O})_6^{3+}] \cdot [\text{en}]^3}$$

$$\log \beta_3 = 19.4 \text{ (24 } ^\circ\text{C; 1.00M NaCl)} ; \log K_1 = 6.43$$

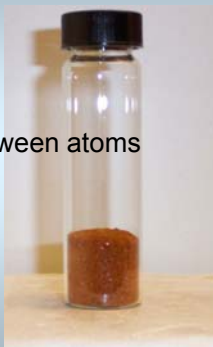
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Other properties

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



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