General and Inorganic Chemistry Department,
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Introduction to Coordination Compounds

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1 Definitions

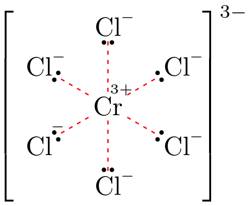
Basic definitions

- The **Coordination Compounds** contain *complex particles*
- The complex particle general formula is as follows:

$$\left[\mathrm{Me}_x^{n+}\mathrm{L}_y^{m-}\right]^{nx-my}, \text{where}$$

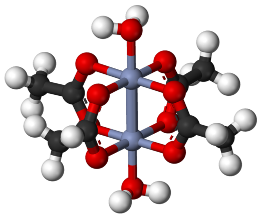
  - Me^{n+} is the **central ion** of metal having **unoccupied orbitals**;
  - L^{m-} is the **ligand**, the molecule or ion having **lone electron pair**.

- Hence, the *coordination bond* is a **dative** bond



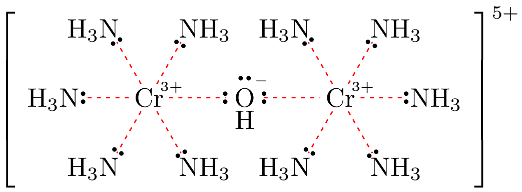
mononuclear

hexachloridochromate (III)



dinuclear cluster

chromium (II) acetate

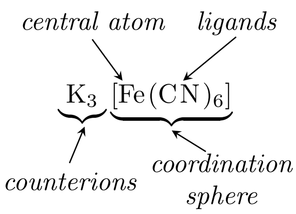


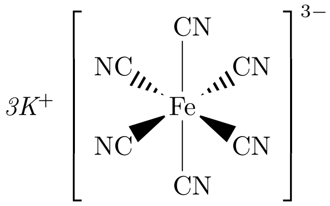
dinuclear bridged

μ-hydroxo-bis(pentaammine)chromium (III)

2 The components of coordination compound

Coordination compounds main components





Potassium hexacyanoferrate (III)

The central atom is a *coordination center*
The *coordination sphere* is a metal complex
The *outer spere* contains *counterions*
The *ligands* are ions or molecules
The *coordination number* (C.N.) is the total number of neighbors of a central atom
C.N. can be from 1 to 12; in the most of the cases is equal to 4 or 6. It very often appears to be *two times more* than total charge of the complex particle
The *denticity* of the ligand is the number of places that it occupies in the coordination sphere:
*mono*dentate ligands:
$:\ddot{\mathrm{Cl}}:^-$, $\ddot{\mathrm{N}}H_3$, $H_2\ddot{\mathrm{O}}$, ONO^-, $\ddot{\mathrm{C}}\equiv\mathrm{N}^-$, $\ddot{\mathrm{S}}\mathrm{CN}^-$, etc
only one atom can coordinate the central ion;
*poly*dentate ligands:
$^-\ddot{\mathrm{O}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\ddot{\mathrm{O}}^-$, $H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$ etc
more than one atom coordinates the central ion.

3 Coordination compounds nomenclature

Coordination compounds nomenclature

- A *cation* must be called first then anion
  - $[Ni(NH_3)_6]Cl_2$ – *hexaamminenickel (II)* chloride
  - $K_2[Ni(CN)_4]$ – *potassium* tetracyanonickelate (II)
- 2 – di, 3 – tri, 4 – tetra, 5 – penta, 6 – hexa, 7 – hepta
- Ligands: should be mentioned in alphabetical order:
  - $K[Pt(NH_3)Br_5]$ – potassium amminepentabromidoplatinate (IV)
  - $[Co(H_2O)_5Cl]Cl_2$ – pentaaquamonochloridocobalt (III) chloride
- *Oxidation state* of the central atom
  - $K_4[Fe(CN)_6]$ – potassium hexacyanoferrate *(II)*
  - $K_3[Fe(CN)_6]$ – potassium hexacyanoferrate *(III)*
- Structure is connected with the name:

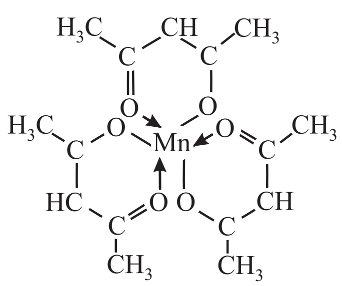
  potassium hexa cyano ferrate (III) $K_3[Fe(CN)_6]$

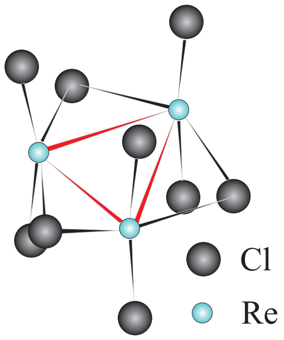
4 Classification

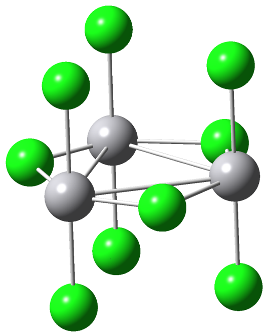
Classification of coordination compounds

- By class: acid, base or salt
  $H[AuCl_4]$, $[Ag(NH_3)_2]OH$, $[Cr(H_2O)_6]Cl_3$
- By the nature of ligand:
  - aquacomplexes ($[Cu(H_2O)_4]^{2+}$)
  - ammincomplexes ($[Ag(NH_3)_2]^{+}$)
  - hydroxocomplexes ($[Al(OH)_6]^{3-}$)
- By charge: cation, anion, neutral
  $[Co(NH_3)_6]Cl_3$, $Li[AlH_4]$, $[Co(NH_3)_3Cl_3]$

- By central atoms number: mononuclear, polynuclear (bridged or cluster complexes)







5 Dissociation

Dissociation of complex compounds

- Dissociation occurs in two stages:
  - "primary": $K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$
  - "secondary": $[Fe(CN)_6]^{4-} \rightleftarrows Fe^{2+} + 6CN^-$
- Dissociation of the complex is an equilibrium:
  - $K_{\text{ins}} = \dfrac{c(Fe^{2+})c^6(CN^-)}{c([Fe(CN)_6]^{4-})}$
  - $K_{\text{st}} = \dfrac{c([Fe(CN)_6]^{4-})}{c(Fe^{2+})c^6(CN^-)}$ is recommended by IUPAC
  - $K_{\text{st}} = 1/K_{\text{ins}}$
- The more the K_{st} the more stable complex is
- Step-by-step dissociation
  - $[Ag(NH_3)_2]^+ \rightleftarrows [Ag(NH_3)]^+ + NH_3, \beta_1 = \frac{c([Ag(NH_3)]^+)c(NH_3)}{c([Ag(NH_3)_2]^+)}$
  - $[Ag(NH_3)]^+ \rightleftarrows Ag^+ + NH_3, \beta_2 = \frac{c(Ag^+)c(NH_3)}{c([Ag(NH_3)]^+})$
  - $[Ag(NH_3)_2]^+ \rightleftarrows Ag^+ + 2NH_3, K_{\text{ins}} = \beta_1 \cdot \beta_2$

6 Some reactions

Coordination compounds: some reactions

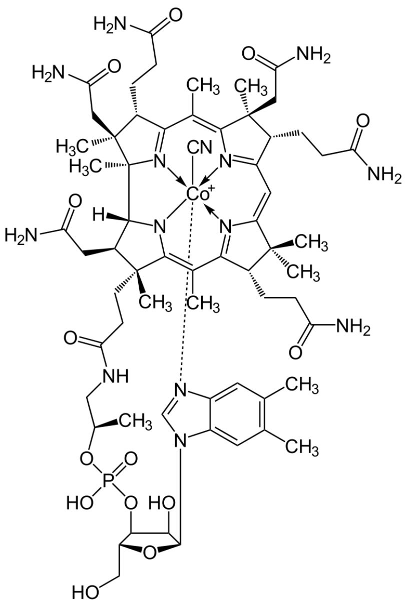
- Formation of the complexes

- $AgCl + 2NH_3 = [Ag(NH_3)_2]Cl$
- $AuCN + KCN = K[Au(CN)_2]$

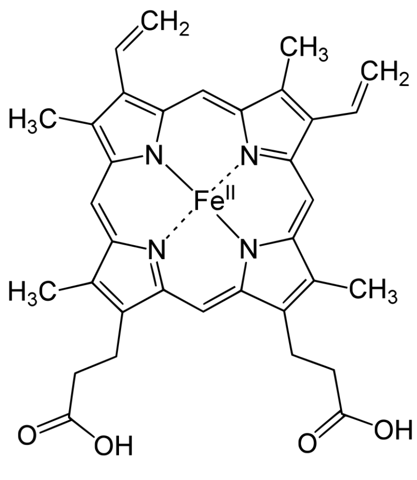
- Reaction to Fe^{2+} and Fe^{3+} cations:
  - $FeSO_4 + K_3[Fe(CN)_6] = \underbrace{KFe[Fe(CN)_6]\downarrow}_{\text{Turnbull's blue}} + 2K_2SO_4$
  - $FeCl_3 + K_4[Fe(CN)_6] = \underbrace{KFe[Fe(CN)_6]\downarrow}_{\text{Prussian blue}} + 3KCl$
- Bi^{3+} gives a precipitate with KI that dissolves in excess amount of precipitant
  - $BiCl_3 + 3KI = BiI_3\downarrow + 3KCl$
  - $BiI_3 + KI = K[BiI_4]$
- Silver halogenides separation
  - $AgCl + 2NH_3 = [Ag(NH_3)_2]Cl$
  - $AgBr, AgI + 2NH_3 \nrightarrow$
  - $AgHal + 2Na_2S_2O_3 = Na_3[Ag(S_2O_3)_2] + NaHal$

7 Famous complexes

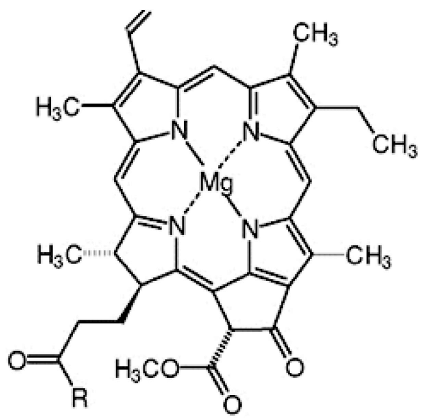
Famous complexes



Cyanocobalamin (B12)



Hemoglobine heme



Chlorophyll

8 Task example

- *Does the* CdS *precipitate will form, if some volume of 0.1 M solution of* Na_2S *will be added to the equal volume of 0.1 M* $K_2[Cd(CN)_4]$ *solution?*
- Condition of sedimentation: $c(Cd^{2+})c(S^{2-}) > K_S(CdS) = 8 \cdot 10^{-27}$
- It's easy to determine $c(S^{2-})$ from $Na_2S \rightarrow 2Na^+ + S^{2-}$
  $c(S^{2-}) = 1/2\ c_{st}(Na_2S) = 0.05$ M (because of mixing dilution)
- $c(Cd^{2+})$ can be found using scheme $[Cd(CN)_4]^{2-} \rightleftarrows Cd^{2+} + 4CN^-$

	$[Cd(CN)_4]^{2-}$	Cd^{2+}	CN^-
c_{st}	0.05	–	–
c_{rctd}	x	–	–
c_{frmd}	–	x	$4x$
c_{eq}	$0.05 - x$	x	$4x$

$K_{st}([Cd(CN)_4]^{2-} = 1.3 \cdot 10^{17}$

$\frac{c([Cd(CN)_4]^{2-})}{c(Cd^{2+})c^4(CN^-)} = 1.3 \cdot 10^{17}$

$\frac{0.05 - x}{x \cdot (4x)^4} = 1.3 \cdot 10^{17}$

If $x \ll 0,05$ *then*

$256x^5 = 3.9 \cdot 10^{-19}$

- $x = c(Cd^{2+}) = 6.9 \cdot 10^{-5}$
- $c(Cd^{2+})c(S^{2-}) = 6.9 \cdot 10^{-5} \cdot 0.05 = 3.5 \cdot 10^{-6} > K_S$
- The conclusion is that precipitate will appear