9. Chemistry of the \(d\)-Block Elements

The \(d\)-Block Elements

http://www.chemsoc.org/viselements/pages/portable fla.htm

9. Chemistry of the \(d\)-Block Elements

The \(d\)-Block Elements...my personal favorites
9. Chemistry of the \(d\)-Block Elements

The \(d\)-Block Elements... my personal favorites

Prof. Karl Wieghardt
Max-Planck-Institute
for Bioinorganic Chemistry
Muelheim/Germany

9. Chemistry of the \(d\)-Block Elements

Alfred Werner - Founder of Coordination Chemistry

"Dot" Representation:

- Pentachlorophosphorous \(\text{PCl}_5\)
- \(\text{PCl}_3 \cdot \text{Cl}_2\)
- Copper(II) Sulfate Pentahydrate
  \(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}\)
- Hex(a)ammin Cobalt(III) Chloride
  \(\text{CoCl}_3 \cdot 6\text{NH}_3\)

George B. Kauffman
Alfred Werner
Founder of Coordination Chemistry

Springer-Verlag Berlin Heidelberg New York 1966
### Alfred Werner - Founder of Coordination Chemistry

#### Jørgensen

- \( \text{Co(NH}_3\text{)}_6\text{Cl} \)
- \( \text{Co(NH}_3\text{)}_5\text{Cl} \)
- \( \text{Co(NH}_3\text{)}_4\text{(Cl)}_2\text{Cl} \)
- \( \text{Co(NH}_3\text{)}_4\text{(Cl)}_2\text{Cl} \)

#### Werner

- \([\text{Co(NH}_3\text{)}_6\text{Cl}]_3\)
- \([\text{Co(NH}_3\text{)}_5\text{Cl}]_2\)
- \([\text{Co(NH}_3\text{)}_4\text{(Cl)}_2\text{Cl}]_2\text{Cl} \)
- \([\text{Co(NH}_3\text{)}_4\text{(Cl)}_2\text{Cl}]_2\text{Cl} \)

---

### Chemistry of the \(d\)-Block Elements

**Alfred Werner – Founder of Coordination Chemistry**

<table>
<thead>
<tr>
<th>Prefix</th>
<th>Color</th>
<th>Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>luteo</td>
<td>yellow</td>
<td>(\text{Co}^{II}\text{Cl}_3 \cdot 6\text{NH}_3)</td>
</tr>
<tr>
<td>purpureo</td>
<td>red</td>
<td>(\text{Co}^{II}\text{Cl}_3 \cdot 5\text{NH}_3)</td>
</tr>
<tr>
<td>praseo</td>
<td>green</td>
<td>(\text{Co}^{II}\text{Cl}_3 \cdot 4\text{NH}_3)</td>
</tr>
<tr>
<td>violeo</td>
<td>violet</td>
<td>(\text{Co}^{II}\text{Cl}_3 \cdot 4\text{NH}_3)</td>
</tr>
</tbody>
</table>
9. Chemistry of the d-Block Elements

Alfred Werner - Founder of Coordination Chemistry

cis- and trans - Tetrarminedichlorocobalt (III), \([\text{Co(NH}_3\text{)}_4\text{Cl}_2]^{2-}\)

Hexagonal (three isomers)

Hexagonal pyramidal (three isomers)

Trigonal prismatic (three isomers)

Trigonal antiprismatic (three isomers)
9. Chemistry of the d-Block Elements

Alfred Werner - Founder of Coordination Chemistry

Cisplatin was approved by the FDA for the treatment of genitourinary tumors in 1978. Since then, Michigan State has collected over $160 million in royalties from cisplatin and a related drug, carboplatin, which was approved by the FDA in 1989 for the treatment of ovarian cancers.

"Testicular cancer went from a disease that normally killed about 80% of the patients, to one which is close to 95% curable. This is probably the most exciting development in the treatment of cancers that we have had in the past 20 years. It is now the treatment of first choice in ovarian, bladder, and osteogenic sarcoma [bone] cancers as well."

—Barnett Rosenberg, who led the research group that discovered cisplatin, commenting on the impact of cisplatin in cancer chemotherapy
First non-carbon containing chiral compound: \( \text{Hexol} \left[ \text{Co} \left( \text{OH} \right)_2 \text{Co} \left( \text{NH}_3 \right)_2 \right] \left( \text{SO}_4 \right)_3 \), resolved in 1914 with (+)-bromocamphorsulphonate

definitive proof of Alfred Werner's octahedron model
\( \rightarrow \) Synthesis of optically active complexes!
### 9. Chemistry of the d-Block Elements

#### Coordination Chemistry - Nomenclature

**TABLE 9-2** Common Monodentate Ligands

<table>
<thead>
<tr>
<th>Common Name</th>
<th>IUPAC Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>fluoro</td>
<td>fluoro</td>
<td>F</td>
</tr>
<tr>
<td>chloro</td>
<td>chloro</td>
<td>Cl</td>
</tr>
<tr>
<td>nitro</td>
<td>nitro</td>
<td>NO</td>
</tr>
<tr>
<td>acido</td>
<td>acido</td>
<td>HC</td>
</tr>
<tr>
<td>cyan</td>
<td>cyanide</td>
<td>CN</td>
</tr>
<tr>
<td>thiocyanate</td>
<td>thiocyanate</td>
<td>SCN</td>
</tr>
<tr>
<td>hydroxide</td>
<td>hydroxide</td>
<td>OH</td>
</tr>
<tr>
<td>aqua</td>
<td>aqua</td>
<td>H₂O</td>
</tr>
<tr>
<td>carbon</td>
<td>carbonyl</td>
<td>CO</td>
</tr>
<tr>
<td>nitrate</td>
<td>nitrate</td>
<td>NO₃</td>
</tr>
<tr>
<td>amine</td>
<td>amino</td>
<td>NH₂</td>
</tr>
<tr>
<td>ethylenediamine</td>
<td>1,2-ethylenediamine</td>
<td>NH-NH</td>
</tr>
<tr>
<td>diethylenetriamine</td>
<td>1,3,5-triaza-pentane</td>
<td>NH-NH-NH</td>
</tr>
<tr>
<td>triethylenetramine</td>
<td>1,4,7-triaminerubicaine</td>
<td>NH-NH-NH-NH</td>
</tr>
<tr>
<td>tetraethylenepentamine</td>
<td>1,6,10,14-tetraazapentadecane</td>
<td>NH-NH-NH-NH-NH</td>
</tr>
<tr>
<td>pentaethyleneglycol</td>
<td>1,5,10,15,20-pentaazapentadecahydrododecanine</td>
<td>NH-NH-NH-NH-NH-NH</td>
</tr>
<tr>
<td>hexaethyleneglycol</td>
<td>1,7,12,18,23,29-hexaazahexaoctaheptadecane</td>
<td>NH-NH-NH-NH-NH-NH-NH</td>
</tr>
</tbody>
</table>

**TABLE 9-3** Common Chelating Amines

<table>
<thead>
<tr>
<th>Common Name</th>
<th>IUPAC Name</th>
<th>Abbreviation</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>monodentate</td>
<td>amine, methylamine</td>
<td></td>
<td>NH₃, CH₃NH₂</td>
</tr>
<tr>
<td>bidentate</td>
<td>ethylenediamine</td>
<td></td>
<td>NH₂-NH₂</td>
</tr>
<tr>
<td>tridentate</td>
<td>triethylenetramine</td>
<td></td>
<td>NH₂-NH-NH₂</td>
</tr>
<tr>
<td>tetra dentate</td>
<td>tetraethylenepentamine</td>
<td></td>
<td>NH₂-NH-NH-NH-NH₂</td>
</tr>
<tr>
<td>penta dentate</td>
<td>pentaethyleneglycol</td>
<td></td>
<td>NH₂-NH-NH-NH-NH-NH-NH₂</td>
</tr>
<tr>
<td>hexa dentate</td>
<td>hexaethyleneglycol</td>
<td></td>
<td>NH₂-NH-NH-NH-NH-NH-NH-NH-NH₂</td>
</tr>
</tbody>
</table>

**TABLE 9-4** Coordination Compounds

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaN₃</td>
<td>[Ni(N₃)₄]²⁺</td>
</tr>
<tr>
<td>[Ni(CN)₄]²⁻</td>
<td></td>
</tr>
<tr>
<td>[Ni(H₂O)₆]²⁺</td>
<td></td>
</tr>
<tr>
<td>[Ni(NH₃)₆]²⁺</td>
<td></td>
</tr>
<tr>
<td>[Ni(C₂H₄)₂]²⁻</td>
<td></td>
</tr>
<tr>
<td>[Ni(C₆H₅NH₂)₂]²⁻</td>
<td></td>
</tr>
</tbody>
</table>
Coordination Chemistry - Nomenclature

**TABLE 9.1**

<table>
<thead>
<tr>
<th>Common Name</th>
<th>HPLC Name</th>
<th>Abbreviation</th>
<th>Formulas and Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetylacetonate</td>
<td>2,4-pentanedione</td>
<td>acac</td>
<td>CH$_2$C(O)OCH$_2$</td>
</tr>
<tr>
<td>2,2'-bipyridine</td>
<td>2,2'-bipyridyl</td>
<td>bpy</td>
<td>C$_2$H$_6$N$_2$</td>
</tr>
<tr>
<td>1,10-phenanthroline</td>
<td>1,10-phenanthroline</td>
<td>phen, phen</td>
<td>C$_2$H$_8$N$_2$</td>
</tr>
<tr>
<td>oxalate</td>
<td>oxalo</td>
<td>ox</td>
<td>C$_2$H$_2$O$_4$</td>
</tr>
<tr>
<td>dicyclohexanoanthracene</td>
<td>dicyclohexanoanthracene</td>
<td>dca</td>
<td>5,5-$C_7H_8$</td>
</tr>
<tr>
<td>1,2-bis(diphenylphosphinophenyl)benzene</td>
<td>1,2-bis(diphenylphosphinophenyl)benzene</td>
<td>dppp</td>
<td>P$_2$N$_2$(Ph$_2$P)$_2$</td>
</tr>
</tbody>
</table>

9. Chemistry of the \(d\)-Block Elements

Coordination Chemistry - Nomenclature
9. Chemistry of the d-Block Elements

Coordination Chemistry - Nomenclature

1. The positive ion (cation) comes first, followed by the negative ion (anion). This is also the common order for simple salts.
   
   **Examples:** diamminesilver(I) chloride, [Ag(NH₃)₂]Cl
   potassium hexacyanoferrate(III), K₃[Fe(CN)₆]

2. The inner coordination sphere is enclosed in square brackets in the formula. Within the coordination sphere, the ligands are named before the metal, but in formulas the metal ion is written first.
   
   **Examples:** tetraamminecopper(II) sulfate, [Cu(NH₃)₄]SO₄
   hexaaquamagnesium(II) chloride, [Co(NH₃)₆]Cl₂

3. The number of ligands of one kind is given by the following prefixes. If the ligand name includes these prefixes or is complicated, it is set off in parentheses and the second set of prefixes is used.

   - 2: di, bis
   - 3: tri, tris
   - 4: tetra, tetrakis
   - 5: penta, pentakis
   - 6: hexa, hexakis
   - 7: hepta, heptakis
   - 8: octa, octakis
   - 9: nona, nonakis
   - 10: deca, decakis

   **Examples:** dichlorobis(oethylenediamine)cobalt(III),
   [Co(NH₃)₂(CH₂CH₂NH₃)₂][Cl₂]
   tris(bipyridyl)iron(II), [Fe(NH₃)₃C₆H₄(NH₂)₃]⁺
9. Chemistry of the d-Block Elements

Coordination Chemistry - Nomenclature

1. Ligands are named in alphabetical order (according to the name of the ligand, not the prefix), although exceptions to this rule are common. An earlier rule gave anionic ligands first, then neutral ligands, each listed alphabetically.

   Examples: tetramminechloroplatinate(II), (Co(NH)_3Cl)_2^-
              (tetrammine) is alphabetized by o and dihalo by c, not by the prefixes.
              amminebromochlorometallatoargentate(II),
              Pt(NH)_3BrCl(NH_3)_2

2. Anionic ligands are given an -ate suffix. Neutral ligands retain their usual name.

   Examples:
   chloro, Cl^-
   bromo, Br^-
   sulfato, SO_4^{2-}
   aqua, H_2O
   methylamino, CH_3NH_2
   ammine, NH_3 (the double m distinguishes NH_3 from alkylamines)

6. Two systems exist for designating charge or oxidation number:
   a. The Stock system puts the calculated oxidation number of the metal ion as a Roman numeral in parentheses after the name of the metal. This is the more common convention, although there are cases in which it is difficult to assign oxidation numbers.
   b. The Feigl-Brayss system puts the charge on the coordination sphere in parentheses after the name of the metal. This convention is used by Chemical Abstracts and offers an unambiguous identification of the species.

   In either case, if the charge is negative, the suffix -ate is added to the name of the coordination sphere.

   Examples:
   tetraammineplatinum(II) or tetraammineplatinum(II),
   [Pt(NH_3)_4]^2+
   tetrachloroplatinate(II) or tetrachloroplatinate(II), [PtCl_4]^2-
   hexachloroplatinate(IV) or hexachloroplatinate(IV), [PtCl_6]^{3-}
9. Chemistry of the d-Block Elements

Coordination Chemistry - Nomenclature

7. The prefixes *cis* - and *trans* - designate adjacent and opposite geometric locations. Examples are in Figures 9-1 and 9-5. Other prefixes are used as well and will be introduced as needed in the text.

Examples: *cis* - and *trans*-diaminedichloroplatinum(II), \([\text{PtCl}_2(\text{NH}_3)_2]\)
*cis* - and *trans*-tetraaminedichlorocobalt(III), \([\text{CoCl}_2(\text{NH}_3)_4]\)^2+

8. Bridging ligands between two metal ions as in Figures 9-2 and 9-6 have the prefix \(\mu\)-

Examples: \(\mu\)-tris(tetramine-\(\mu\)-hydroxy)cobalt(6+)
\([\text{Co}(\text{NH}_3)_3(\text{OH})\text{Co}(\text{NH}_3)_3]^2+\)
\(\mu\)-amido-\(\mu\)-hydroxybis(tetrammine)cobalt(4+)
\([\text{Co}(\text{NH}_3)_4(\text{NH}_2)(\text{OH})(\text{NH}_3)_3]^2+\)

9. When the complex is negatively charged, the names for the following metals are derived from the sources of their symbols, rather than from their English names:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>iron</td>
<td>ferrate</td>
</tr>
<tr>
<td>silver</td>
<td>argentate</td>
</tr>
<tr>
<td>lead</td>
<td>plumbate</td>
</tr>
<tr>
<td>gold</td>
<td>aurate</td>
</tr>
<tr>
<td>tin</td>
<td>stannate</td>
</tr>
</tbody>
</table>

Examples: tetrachloroferrate(III) or tetrachloroferrate\((1-)\), \([\text{FeCl}_4]\)^- 
dicyanoaurate(1) or dicyanoaurate\((1-)\), \([\text{Au(CN)}_2]\)^-
Coordination Chemistry - Nomenclature

IUPAC Rules for complex formula:

- Coordination complex in square brackets, charge superscripted
- Central atom in front of ligands
- Anionic in front of neutral ligands
- Multiple atoms & abbrev. ligands in round brackets
- Oxidation number superscripted at central atom

\[ \text{[Cr}^{III}(\text{NCO})_4(\text{NH}_3)_2]^- \quad \text{[Pt}^{II}\text{BrCl(NO}_2)(\text{NH}_3)]^- \quad \text{[Pt}^{IV}\text{BrCl(NO}_2)(\text{py})(\text{NH}_3)] \]

IUPAC Rules for complex name:

Main Difference: ligands first, followed by central atom

- Ligands in alphabetical order in front of central atom/ion
- Specification of oxidation number (Roman numerals) of the central atom (or the charge number in Arabic numerals after the name of the central atom)
- Name of anionic ligands close with "o", neutral ligands in round brackets (except: ammine, aqua, carbonyl, nitrosyl)
9. Chemistry of the d-Block Elements

Coordination Chemistry - Nomenclature

K₃[Fe(CN)₆] Potassium-hexacyanoferrate(III) or Potassium-hexacyanoferrate(3-) (or Tripotassium-hexacyanoferrate)

K₂[PtCl₄] Potassium-tetrachloroplatinate(II)

Na₂[Fe(CO)₄] Disodium-tetracarbonylferrate

[Co(H₂O)₂(NH₃)₄]Cl₃ Tetra(a)mmindiaquacobalt(3+) chloride
9. Chemistry of the d-Block Elements

Coordination Chemistry - Nomenclature

Diamminediaqua-dicyanocobalt(III)

Carbonylichlorohydridotris(triphenylphosphine)ruthenium(II)

Tris(ethylenediamine)-cobalt(III) pentacyanonicelate(II)

Coordination Chemistry - Isomers

Priority Rules: ...remember Cahn-Ingold-Prelog?

practice...
9. Chemistry of the \textit{d} -Block Elements

**Coordination Chemistry - Isomers**

... in four-coordinate square-planar complexes:

\[
\begin{align*}
\text{cis-} & \quad & \text{trans-} \\
\text{H}_3\text{N} & \quad \text{Pt} & \quad \text{Cl} \\
\text{H}_3\text{N} & \quad \text{Pt} & \quad \text{Cl} \\
\text{Cl} & \quad \quad & \text{NH}_3
\end{align*}
\]

and chiral isomers in square planar complexes

chirality (chiral center) can be incorporated ligand

---

9. Chemistry of the \textit{d} -Block Elements

**Coordination Chemistry - Isomers**

... in six-coordinate octahedral complexes:

special case of \textit{cis-} \& \textit{trans-} isomers:

\[
\begin{align*}
\text{carboxyl group} & \quad \text{trans to tertiary N} \\
\text{carboxyl group} & \quad \text{cis to tertiary N}
\end{align*}
\]
9. Chemistry of the d-Block Elements

**Coordination Chemistry - Isomers**

...in six-coordinate octahedral complexes:

in addition to cis- & trans- and chiral (Chapter 4) isomers:

fac- and mer-isomers more obvious with poly (tri-)dentate ligands such as:

- tacn, tp- (fac)
- terpy (mer)

9. Chemistry of the d-Block Elements

**Coordination Chemistry - Isomers**

...in six-coordinate octahedral complexes:

special case of chirality in en or tacn complexes:

- tacn, δδδ or λλλ
- en
9. Chemistry of the d-Block Elements

Coordination Chemistry - Isomers

Hydrate Isomerism

CrCl$_3$ • 6H$_2$O (dark green, mostly trans-[CrCl$_2$(H$_2$O)$_4$]Cl)

- violet: [Cr(H$_2$O)$_6$]Cl$_3$
- blue-green: [CrCl(H$_2$O)$_5$]Cl$_2$ • H$_2$O
- dark green: [CrCl$_2$(H$_2$O)$_4$]Cl • 2H$_2$O*
- yellow-green: [CrCl$_3$(H$_2$O)$_3$] in conc. HCl

Ionization Isomerism

[CoCl(NH$_3$)$_4$(H$_2$O)]Br$_2$ and [CoBr$_2$(NH$_3$)$_4$]Cl • H$_2$O (also hydrate isomers)

[Co(SO$_4$)(NH$_3$)$_5$]NO$_3$ and [Co(NO$_3$)(NH$_3$)$_5$]SO$_4$

[CoCl(NO$_2$)(NH$_3$)$_4$]Cl and [CoCl$_2$(NH$_3$)$_6$]NO$_2$
Coordination Chemistry - Isomers

Coordination Isomerism

\[
\text{[Pt(NH}_3\text{)_4][PtCl}_6\text{] (Magnus' green salt)}
\]

different metal ions in different oxidation states:

\[
\text{[Co(en)_3][Cr(CN)_6] and [Cr(en)_3][Co(CN)_6]}
\]

\[
\text{[Pt(NH}_3\text{)_4][PtCl}_6\text{] and [PtCl}_2\text{(NH}_3\text{)}_4[PtCl}_4\text{]}
\]

Linkage (ambidentate) Isomerism

\[
\begin{align*}
\text{As(C}_6\text{H}_5\text{)}_3 \quad \text{Solvents of low} & \quad \text{As(C}_6\text{H}_5\text{)}_3 \quad \text{Solvents of high} \\
\text{NCS} \quad \text{dielectric constant} & \quad \text{SCN} \quad \text{dielectric constant}
\end{align*}
\]

stable form

\[
\begin{align*}
\text{[O-N-Ru(NO)}_2\text{(OH)}\text{]}^2- & \quad \text{[N-O-Ru(NO)}_2\text{(OH)}\text{]}^2-
\end{align*}
\]
Linkage (ambidentate) Isomerism

iso(thiocyanato)thiocyanato (1-diphenylphosphine-3, dimethylaminepropane)palladium(II)

free rotation
large steric effect

Chapter 10
Coordination Chemistry - Bonding in TM Complexes
Ligand Fields & Ligand Strengths
High-Spin & Low-Spin Complexes

Chapter 16
Coordination Chemistry - Some exciting bioinorganic case studies