Chemistry of the d-Block Elements

History:

Louis Nicolas Vauquelin

Leopold Gmelin

Chemistry of the d-Block Elements

History:

Louis Nicolas Vauquelin
1813

Gmelin
1822
History:

1844: Peyrone's Chloride
\[\text{PtCl}_2(\text{NH}_3)_2\] -- note! same formula! --

1844: Reiset
\[\text{PtCl}_2(\text{NH}_3)_2\]
(isomers are super-important in chemistry!)

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

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.

Prof. Barnett Rosenberg, MSU
(Prof. S.J. Lippard, MIT)

Newest generation:
Chemistry of the d-Block Elements

Cisplatin acts by cross-linking DNA in several different ways, making it impossible for rapidly dividing cells to duplicate their DNA for mitosis. The damaged DNA sets off DNA repair mechanisms, which activate apoptosis when repair proves impossible. The trans isomer does not have this pharmacological effect.

B. Rosenberg et al. in Nature 1965, 205, 698

Stephen J. Lippard et al. in Nature (1999), 399, 708 - 712

SUMMARY: The anticancer activity of cis-diaminedichloroplatinum(II) (cisplatin) arises from its ability to damage DNA, with the major adducts formed being intrastrand d(GpG) and d(ApG).

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Another success story at the HEART of coordination chemistry: CardioLite

"Davison realized that fundamental coordination chemistry would shed light on the chemical characteristics of the element technetium and that these basic chemical characteristics could be translated into the rational design of new radiopharmaceuticals," Orvig notes in the article. He calls Davison "one of the fathers of medicinal inorganic chemistry."

Prof. Chris Orvig, University of British Columbia

Alan Davison, MIT (???)
Another success story at the HEART of coordination chemistry: Cardiolite

The d-Block Elements

http://www.chemsoc.org/viselements/pages/pertable_fla.htm
The d-Block Elements...my personal favorites

Prof. Karl Wieghardt
Max-Planck-Institute
for Bioinorganic Chemistry
Muelheim/Germany
The Werner & Jørgensen Controversy

Alfred Werner — Founder of Coordination Chemistry

"Dot" Representation:

- Pentachlorophosphorous \( \text{PCl}_5 \)
- \( \text{PCl}_3 \cdot \text{Cl}_2 \)
- Copper(II) Sulfate Pentahydrate \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \)
- Copper(II) Acetate Hydrate \( \text{Cu(CH}_3\text{COO)}_2 \cdot \text{H}_2\text{O} \)
- Hex(a)ammin Cobalt(III) Chloride \( \text{CoCl}_3 \cdot 6\text{NH}_3 \)
Alfred Werner – Founder of Coordination Chemistry

Copper(II) Acetate Hydrate
Cu(CH₃COO)₂ • H₂O

Hex(a)ammin Cobalt(III) Chloride
CoCl₃ • 6NH₃
Alfred Werner – Founder of Coordination Chemistry

Hex(a)ammin Cobalt(III) Chloride
CoCl₃ • 6NH₃

<table>
<thead>
<tr>
<th>Prefix</th>
<th>Color</th>
<th>Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>luteo</td>
<td>yellow</td>
<td>Co³⁺Cl₃⁻ • 6NH₃</td>
</tr>
<tr>
<td>purpureo</td>
<td>red</td>
<td>Co³⁺Cl₃⁻ • 5NH₃</td>
</tr>
<tr>
<td>praseo</td>
<td>green</td>
<td>Co³⁺Cl₃⁻ • 4NH₃</td>
</tr>
<tr>
<td>violeo</td>
<td>violet</td>
<td>Co³⁺Cl₃⁻ • 4NH₃</td>
</tr>
</tbody>
</table>

Alfred Werner – Founder of Coordination Chemistry

Chemistry of the d-Block Elements

Alfred Werner’s Kollektion (8000+ Komplexe!) & die „Katakomben“ an der Universität Zürich
Alfred Werner – Founder of Coordination Chemistry

Jørgensen
\[
\begin{align*}
\text{Co} & \text{–NH}_3\text{–Cl} \\
\text{NH}_3 & \text{–NH}_3\text{–NH}_3\text{–NH}_3\text{–NH}_3\text{–Cl} \\
\text{Co} & \text{–NH}_3\text{–Cl} \\
\text{NH}_3 & \text{–NH}_3\text{–NH}_3\text{–NH}_3\text{–NH}_3\text{–Cl} \\
\text{Co} & \text{–Cl} \\
\text{NH}_3 & \text{–NH}_3\text{–NH}_3\text{–NH}_3\text{–Cl} \\
\text{Co} & \text{–Cl} \\
\text{NH}_3 & \text{–NH}_3\text{–NH}_3\text{–Cl}
\end{align*}
\]

Werner
\[
\begin{align*}
\text{[Co(NH}_3\text{)\textsubscript{6}]Cl}_3 \\
\text{[Co(NH}_3\text{)\textsubscript{5}Cl]Cl}_2 \\
\text{[Co(NH}_3\text{)\textsubscript{4}(Cl)\textsubscript{2}]Cl} \\
\text{2 isomers!} \\
\text{[Co(NH}_3\text{)\textsubscript{4}(Cl)\textsubscript{2}]Cl}
\end{align*}
\]

Chemistry of the d-Block Elements

Alfred Werner – Founder of Coordination Chemistry

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>No. of Isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>&amp;Nabla;NO\textsubscript{3} &amp; &amp;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&amp;Nabla;NO\textsubscript{2} &amp; &amp;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&amp;Nabla;NO\textsubscript{2} &amp; &amp;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&amp;Nabla;NO\textsubscript{2} &amp; &amp;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&amp;Nabla;NO\textsubscript{2} &amp; &amp;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&amp;Nabla;NO\textsubscript{2} &amp; &amp;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&amp;Nabla;NO\textsubscript{2} &amp; &amp;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Constitution of each(III) coordination compounds

Alfred Werner – Leitfähigkeit (Kohlrausch’s Prinzip, Konstitution)

C. Kobaltreihe

Alfred Werner & Arturo Miolati (1893 – 1896)

Chemistry of the d-Block Elements

Alfred Werner – Isomere (Konfiguration)

cis- and trans - Tetraminnedichlorocobalt (II), \([\text{Co(NH}_3\text{)}_4\text{Cl}_2]^+\)

Hexagonal (three isomers)

Hexagonal pyramidal (three isomers)
Alfred Werner – Founder of Coordination Chemistry

Chemistry of the d-Block Elements

Trigonal prismatic (three isomers)

Trigonal antiprismatic (three isomers)

Octahedral (two isomers)

cis- and trans - Diamminedichloroplatinum (II): [PtCl₂(NH₃)₂]
A Sidenote: Serendipity in Chemistry

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.

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First non-carbon containing chiral compound:

Hexol [(Co ((OH)2Co(NH3)4)](SO4)3, resolved in 1914 with (+)-bromocamphorsulphonate

definitive proof of Alfred Werner’s octahedron model

-> Synthesis of optically active complexes!
### 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>fluoride</td>
<td>fluoride</td>
<td>F</td>
</tr>
<tr>
<td>chlorate</td>
<td>chlorate</td>
<td>ClO₄⁻</td>
</tr>
<tr>
<td>nitrate</td>
<td>nitrate</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td>iodate</td>
<td>iodate</td>
<td>I₅O₇⁻</td>
</tr>
<tr>
<td>thiocyanate</td>
<td>thiocyanate</td>
<td>SCN⁻</td>
</tr>
<tr>
<td>dithiocyanate</td>
<td>dithiocyanate</td>
<td>NC₂S₂⁻</td>
</tr>
<tr>
<td>cyanide</td>
<td>cyanide</td>
<td>CN⁻</td>
</tr>
<tr>
<td>hydroxide</td>
<td>hydroxide</td>
<td>OH⁻</td>
</tr>
<tr>
<td>amine</td>
<td>amine</td>
<td>NH₂</td>
</tr>
<tr>
<td>hydrazine</td>
<td>hydrazine</td>
<td>N₂H₂</td>
</tr>
<tr>
<td>ethylenediamine</td>
<td>ethylenediamine</td>
<td>H₂N(CH₂)₂N(H)₂</td>
</tr>
<tr>
<td>phosphine</td>
<td>phosphine</td>
<td>PH₃</td>
</tr>
<tr>
<td>pyridine</td>
<td>pyridine</td>
<td>C₅H₅N</td>
</tr>
<tr>
<td>acetamide</td>
<td>acetamide</td>
<td>CH₃CONH₂</td>
</tr>
<tr>
<td>methyleneamine</td>
<td>methyleneamine</td>
<td>CH₂NH₂</td>
</tr>
<tr>
<td>thioacetamide</td>
<td>thioacetamide</td>
<td>C(S)H₂NH₂</td>
</tr>
</tbody>
</table>

### Coordination Chemistry - Nomenclature

#### TABLE 9-3  Common Chelating Amines

<table>
<thead>
<tr>
<th>Chelating Amines</th>
<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>amine, methylamine</td>
<td>NH₂, CH₃NH₂</td>
<td></td>
</tr>
<tr>
<td>bidentate</td>
<td>ethylenediamine</td>
<td>ethylenediamine</td>
<td>H₂N(CH₂)₂N(H)₂</td>
<td></td>
</tr>
<tr>
<td>tridentate</td>
<td>triethylenetetramine</td>
<td>triethylenetetramine</td>
<td>NH₃·CH₂NH₃</td>
<td></td>
</tr>
<tr>
<td>quadridentate</td>
<td>tetraethylenepentamine</td>
<td>tetraethylenepentamine</td>
<td>NH₃·CH₂NH₃·CH₂NH₃</td>
<td></td>
</tr>
<tr>
<td>pentadentate</td>
<td>pentamethylenediamine</td>
<td>pentamethylenediamine</td>
<td>NH₃·CH₂NH₃·CH₂NH₃·CH₂NH₃</td>
<td></td>
</tr>
<tr>
<td>hexadentate</td>
<td>hexamethylenetetramine</td>
<td>hexamethylenetetramine</td>
<td>NH₃·CH₂NH₃·CH₂NH₃·CH₂NH₃·CH₂NH₃</td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- **NH₃·CH₂NH₃** represents 1,2-ethandiamine or 1,1,1-triamethylethane.
- **NH₃·CH₂NH₃·CH₂NH₃** represents 1,2,3-propanetriamine.
- **NH₃·CH₂NH₃·CH₂NH₃·CH₂NH₃** represents 1,2,3,4-tetraaminobutane.
- **NH₃·CH₂NH₃·CH₂NH₃·CH₂NH₃·CH₂NH₃** represents 1,2,3,4,5-pentamethylenepentane.
- **NH₃·CH₂NH₃·CH₂NH₃·CH₂NH₃·CH₂NH₃·CH₂NH₃** represents 1,2,3,4,5,6-hexamethylenhexane.

---

**Note:** The diagram on the right represents the Coordination Chemistry of the d-Block Elements and shows various molecular structures and isomers.
Coordination Chemistry - Nomenclature

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Shell Source</th>
<th>Abbreviation</th>
<th>Formulas and Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetylacetone</td>
<td>2.4-propanedione</td>
<td>acac</td>
<td>CH_3COCH(OH)_2^-</td>
</tr>
<tr>
<td>2,2'-bipyridine</td>
<td>2,2'-bipyridyl</td>
<td>bipy</td>
<td>N,N,N,N'-tetraakis(pyridin-2-yl)</td>
</tr>
<tr>
<td>1,10-phenanthroline</td>
<td>1,10-phenanthroline</td>
<td>phen</td>
<td>C_{10}H_7N</td>
</tr>
<tr>
<td>oxalate</td>
<td>oxalate</td>
<td>oxalate</td>
<td>C_{2}H_{2}O_{4}^-</td>
</tr>
<tr>
<td>dicyclohexylcarbodimide</td>
<td>dicyclohexylcarbodimide</td>
<td>dchc</td>
<td>5(C_{12}H_{22}N_{2}O_{2})</td>
</tr>
<tr>
<td>1,2-bis(dimethoxyphosphino)</td>
<td>1,2-bis(dimethoxyphosphino)</td>
<td>dipm</td>
<td>P(CH_{3}O)_{2}</td>
</tr>
</tbody>
</table>

Chemistry of the d-Block Elements

Coordination Chemistry - Nomenclature

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Shell Source</th>
<th>Abbreviation</th>
<th>Formulas and Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethylisteronate</td>
<td>dimethylisteronate</td>
<td>dim</td>
<td>C_{6}H_{12}N_{2}O_{2}</td>
</tr>
<tr>
<td>dimethylisteronate</td>
<td>dimethylisteronate</td>
<td>dim</td>
<td>C_{6}H_{12}N_{2}O_{2}</td>
</tr>
<tr>
<td>ethylisobutylm-group</td>
<td>ethylisobutylm-group</td>
<td>ethiob</td>
<td>(CH_{3})<em>{2}CHCH</em>{2}</td>
</tr>
<tr>
<td>ethylisobutylm-group</td>
<td>ethylisobutylm-group</td>
<td>ethiob</td>
<td>(CH_{3})<em>{2}CHCH</em>{2}</td>
</tr>
<tr>
<td>1,2-bis(dimethoxyphosphino)</td>
<td>1,2-bis(dimethoxyphosphino)</td>
<td>dipm</td>
<td>P(CH_{3}O)_{2}</td>
</tr>
<tr>
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<td>1,2-bis(dimethoxyphosphino)</td>
<td>dipm</td>
<td>P(CH_{3}O)_{2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

15
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(NH$_3$)$_2$]Cl
             potassium hexacyanoferrate(III), K$_3$[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(NH$_3$)$_4$]SO$_4$
             hexaaamminecobalt(III) chloride, [Co(NH$_3$)$_6$]Cl$_3$

Chemistry of the d-Block Elements

Coordination Chemistry - Nomenclature

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: dichloro(N,N'-ethylenediamine)cobalt(III),
           [Co(NH$_3$)$_2$-CH$_2$CH$_2$NH$_2$]-Cl$^-$
           tris(bipyridine)iron(II), [Fe(NH$_3$)$_2$C$_5$H$_5$N]$_2$$^+$
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: tetrakis(dimethylglyoximato)nickel(II), (dien(NH₂)₂)²⁺
(tetraammine) is abbreviated by a and dichloro by Cl, not by the prefixes.
Diamminebischloroethylenediammineplatinum(II).
Pd(NH₂)₂(PhCl₂)₂(NH₂)₂

2. Anionic ligands are given an -ate suffix. Neutral ligands retain their usual name. Coordinated water is called aqua and coordinated ammonia is called ammine.

Examples: chloro, Cl⁻ methyamine, CH₃NH₂
bromo, Br⁻ ammine, NH₃ (the double line distinguishes NH₃ from alkylamines)
sulfato, SO₄²⁻
aqua, H₂O

Chemistry of the d-Block Elements

Coordination Chemistry - Nomenclature

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 Fawcett-Basset 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(NH₃)₄]²⁺
tetrachloroplatinate(II) or tetrachloroplatinate(II)
[PtCl₄]²⁻
hexachloroplatinate(IV) or hexachloroplatinate(IV)
[PtCl₆]³⁻
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), [PtCl₂(NH₃)₂]⁺
            cis- and trans-tetraaminedichlorocobalt(III), [CoCl₂(NH₃)₄]⁺

8. Bridging ligands between two metal ions as in Figures 9-2 and 9-6 have the prefix μ-

Examples: tris[tetrammine-μ-dihydroxocobalt]cobalt(III)⁺⁺,
           μ-amido-μ-hydroxo[tetramminecobalt]²⁺⁺
           μ₃-amine[μ₃-amine][μ₃-amine]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:

   iron (Fe)    ferrate               lead (Pb)     plumbate
   silver (Ag)  argentate            tin (Sn)      stannate
   gold (Au)    aurate

Examples: tetrachloroferrate(III) or tetrachloroferrate(III), [FeCl₄]⁻
           dicyanoaurate(I) or dicyanoaurate(I⁻), [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 @ central atom

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)
### Coordination Chemistry - Nomenclature

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₃[Fe(CN)₆]</td>
<td>Potassium-hexacyanoferrate(III) or Potassium-hexacyanoferrate(3-) (or Tripotassium-hexacyanoferrate)</td>
</tr>
<tr>
<td>K₂[PtCl₄]</td>
<td>Potassium-tetrachloroplatinate(II)</td>
</tr>
<tr>
<td>Na₂[Fe(CO)₄]</td>
<td>Disodium-tetracarbonylferrate</td>
</tr>
<tr>
<td>[Co(H₂O)₂(NH₃)₄]Cl₃</td>
<td>Tetraamminediaquacobalt(3+) chloride</td>
</tr>
<tr>
<td>[Ni(H₂O)(NH₃)₄]SO₄</td>
<td>Tetra(a)mminediaquanickel(II) sulfate</td>
</tr>
<tr>
<td>Na₂[OsCl₅N]</td>
<td>Disodium-pentachloronitrido-osmate(VI)</td>
</tr>
<tr>
<td>[CoCl(NO₂)(NH₃)₄]Cl</td>
<td>Tetra(a)mminechloronitrito-cobalt(III) chloride</td>
</tr>
<tr>
<td>[CoCl(NH₂)(en)₂]NO₃</td>
<td>Amidochlorobis(ethylenediamine) cobalt(III) nitrate</td>
</tr>
<tr>
<td>[FeH(CO)₃(NO)]</td>
<td>Tricarbonylhydridonitrosyliron(?)</td>
</tr>
<tr>
<td>[PtCl(NH₂CH₃)(NH₃)]Cl</td>
<td>Amminchlorobis(methylamine) platinum(II) chloride</td>
</tr>
</tbody>
</table>
Coordination Chemistry - Nomenclature

Carbonylchlorohydridotris(triphenylphosphine)ruthenium(II)

Diamminediaqua-dicyanocobalt(III)

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

Chemistry of the d-Block Elements

Coordination Chemistry - Isomers

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

 practice...
Coordination Chemistry - Isomers

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

cis- & trans-

and chiral isomers in square planar complexes

chirality (chiral center) can be incorporated ligand

Coordination Chemistry - Isomers

...in six-coordinate octahedral complexes:

special case of cis- & trans-isomers:

carboxyl group trans to tertiary N
carboxyl group cis to tertiary N
Coordination Chemistry - Isomers

... in six-coordinate octahedral complexes:

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

\[
\text{Facial} \quad \text{Meridional}
\]

\[
\begin{align*}
\text{Facial:} & \quad \text{Co} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{NH}_3 \\
\text{Meridional:} & \quad \text{Co} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{NH}_3
\end{align*}
\]

\[
\begin{align*}
\text{[Co(NH}_3\text{)}_2\text{Cl}_2]} & \quad \text{fac- and mer-isomers more obvious with poly (tri-)dentate ligands such as:} \\
\text{tacn, tsp- (fac)} & \quad \text{or terpy (mer)}
\end{align*}
\]

- tacn
- terpy

Chemistry of the d-Block Elements

Coordination Chemistry - Isomers

... in six-coordinate octahedral complexes:

special case of chirality in en or tacn complexes:

\[
\begin{align*}
\text{en} & \quad \lambda \\
\text{tacn, } & \quad \delta \delta \delta \text{ or } \lambda \lambda \lambda
\end{align*}
\]
Coordination Chemistry - Isomers

Hydrate Isomerism

**CrCl₃ • 6H₂O** (dark green, mostly trans-[CrCl₂(H₂O)₄]Cl)

- Violet: [Cr(H₂O)₆]Cl₃
- Blue-green: [CrCl₂(H₂O)₅]Cl₂ • H₂O
- Dark green: [CrCl₂(H₂O)₄]Cl • 2H₂O*
- Yellow-green: [CrCl₃(H₂O)₃] in conc. HCl

*separation by cation ion exchange chromatography

Ionization Isomerism

- [CoCl(NH₃)₄(H₂O)]Br₂ and [CoBr₂(NH₃)₄]Cl • H₂O (also hydrate isomers)
- [Co(SO₄)(NH₃)₅]NO₃ and [Co(NO₃)(NH₃)₅]SO₄
- [CoCl(NO₂)(NH₃)₄]Cl and [CoCl₂(NH₃)₄]NO₂
Coordination Chemistry - Isomers

Coordination Isomerism

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

different metal ions in different oxidation states:

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

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

Linkage (ambidentate) Isomerism

isothiocyanato thiocyanato (1-diphenylphosphine-3-dimethylaminepropane)palladium(II)

free rotation

large steric effect

Chemistry of the d-Block Elements

Coordination Chemistry – Coordination Numbers & Structures

Notes & Blackboard
Chemistry of the d-Block Elements

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

The Metals $s$-, $p$-, and $d$-Orbitals:

taken from:
Harvey & Porter
"Introduction to Physical Inorganic Chemistry"
Addison-Wesley 1963

Chemistry of the d-Block Elements

The five $d$-orbitals

electron density on the axes!
electron density in between the axes!
Remember???

For example: Nickel \((1s^2)(2s^22p^6)(3s^23p^6)(4s^2)(3d^8)\)

In complexes: \([\text{Ni}^{2+}]\) \((1s^2)(2s^22p^6)(3s^23p^6)(3d^8)\) \(\rightarrow\) unpaired electrons!!!

**For a 3d electron:** \(Z^* = Z - S\)

\[
Z^* = 28 - [18 \times (1.00)] - [7 \times (0.35)] = 7.55
\]

\((1s, 2s, 2p, 3s, 3p)\) \((3d)\)

The 18 electrons in the 1s, 2s, 2p, 3s, and 3p levels contribute 1.00 each (Rule 3b); the other 7 electrons in 3d contribute 0.35 each, and the 4s electrons do not contribute (Rule 2).

**For a 4s electron:** \(Z^* = Z - S\)

\[
Z^* = 28 - [10 \times (1.00)] - [16 \times (0.85)] - [1 \times (0.35)]
\]

\((1s, 2s, 2p)\) \((3s, 3p, 3d)\) \((4s)\)

\[
Z^* = 28 - 23.95 = 4.05 \rightarrow \text{The 4s electrons are held less tightly than the 3d!}
\]

All transition metals loose ns electrons more readily than \((n-1)d\) electron:

- Ti(III): d¹, V(III): d², Mn(II): d⁵, Mn(III): d⁴, Mn(IV): d³, Mn(V): d²
Coordination Chemistry – Magnetism

A) Measurement of Susceptibility by Faraday’s Method
B) Measurement of Magnetization with a SQUID Magnetometer

Principle: In an inhomogeneous field a paramagnetic sample is attracted into the zone with the largest field; a diamagnetic sample is repulsed.

Chemistry of the d-Block Elements

Coordination Chemistry – paired/unpaired d-electrons & magnetism

Measurement of Susceptibility by Faraday’s Method

\[ dF = \frac{1}{2} \mu_0 (\chi - \chi_{med}) \text{grad}(H^2) dv \]

\[ F_z = \mu_0 (\chi - \chi_{med}) vH \frac{dH}{dz} \]

in vacuum or helium:

\[ F_z = \mu_0 \chi_g m \frac{dH}{dz} + F' \]

standard with known \( \chi_g^* \) and \( m^* \)

\[ \chi_M = \chi_g^* \frac{m^*}{(F_z^* - F')(F_z - F')/m} M_0 \]

\[ \chi = \frac{\mu_0 N g^2 \beta^2}{4kT} \]

\[ \chi_M = \frac{\mu_0 N_A g^2 \beta^2}{3kT} \frac{S(S+1)}{S(S+1)} \]
Chemistry of the
d-Block Elements

Coordination Chemistry – molecular magnetism

\[ \mu = 2.828 \, (\chi T)^{1/2} \] (T = Kelvin temperature) The unit of magnetic moment is the Bohr magneton, with 1 \( \mu_B = 9.27 \times 10^{-24} \text{ J/T} \text{ (joules/tesla)}. \)

\[ \mu_{S+L} = g \sqrt{S(S + 1) + \frac{1}{4}L(L + 1)} \]

\( \mu = \) magnetic moment
\( g = \) gyromagnetic ratio (conversion to magnetic moment)
\( S = \) spin quantum number
\( L = \) orbital quantum number

Chemistry of the
d-Block Elements

Coordination Chemistry – molecular magnetism

\[ \mu_S = g \sqrt{S(S + 1)} \]
\[ \mu_S = 2 \sqrt{S(S + 1)} = \sqrt{4S(S + 1)} \]
\[ \mu_S = \sqrt{n(n + 2)} \]
Chemistry of the d-Block Elements

Coordination Chemistry – molecular magnetism

\[ \mu = 2.828 \chi T : (T = \text{Kelvin temperature}) \text{ The unit of magnetic moment is the Bohr magneton, with } 1 \mu_B = 9.27 \times 10^{-24} \text{ J T}^{-1} \text{ (joules/tesla)}. \]

\[ \mu_S = \sqrt{n(n + 2)} \]

<table>
<thead>
<tr>
<th>Ion</th>
<th>n</th>
<th>S</th>
<th>L</th>
<th>(\mu_S)</th>
<th>(\mu_{S+1})</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(^{4+})</td>
<td>1</td>
<td>(\frac{1}{2})</td>
<td>2</td>
<td>1.73</td>
<td>3.00</td>
<td>1.7–1.8</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>1</td>
<td>(\frac{1}{2})</td>
<td>2</td>
<td>1.73</td>
<td>3.00</td>
<td>1.7–2.2</td>
</tr>
<tr>
<td>V(^{3+})</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>2.83</td>
<td>4.47</td>
<td>2.6–2.8</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>2.83</td>
<td>4.47</td>
<td>2.8–4.0</td>
</tr>
<tr>
<td>Cr(^{3+})</td>
<td>3</td>
<td>(\frac{1}{2})</td>
<td>3</td>
<td>3.87</td>
<td>5.20</td>
<td>3.8</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>3</td>
<td>(\frac{1}{2})</td>
<td>3</td>
<td>3.87</td>
<td>5.20</td>
<td>4.1–5.2</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>4.90</td>
<td>5.48</td>
<td>5.1–5.5</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>5</td>
<td>(\frac{1}{2})</td>
<td>0</td>
<td>5.92</td>
<td>5.92</td>
<td>5.9</td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>5</td>
<td>(\frac{1}{2})</td>
<td>0</td>
<td>5.92</td>
<td>5.92</td>
<td>5.9</td>
</tr>
</tbody>
</table>

Chemistry of the d-Block Elements

Coordination Chemistry – Bonding in TM Complexes

Ligand Fields & Ligand Strengths

High-Spin & Low-Spin Complexes

- Shape and Symmetry of Ligand and Metal Orbitals
- d-Orbital Splitting in Transition Metal Complexes:
  1) Nature of the ligand
  2) Symmetry of the Complex
Chemistry of the d-Block Elements

Introduction - History

G. N. Lewis

Nevil Vincent Sidgwick
05. Mai. 1873 – 15. März 1952

Chemistry of the d-Block Elements

Lewis Acid-Base Concept:

- Formation of Complexes via Ion-Ion and/or Ion-Dipole Forces:

\[ \text{Fe}^{2+} + 4 \text{Cl}^- \rightarrow [\text{FeCl}_4]^- \]

\[ \delta^+ \quad \delta^- \quad \text{Fe}^{2+} + 6 \text{H}_2\text{O} \rightarrow [\text{Fe(OH}_2)_6]^{2+} \]

\[ \text{e-hole} \quad \text{e-pair} \quad \text{adduct} \]
Chemistry of the d-Block Elements

Lewis Acid-Base Concept:

- Formation of Complexes via Ion-Ion and/or Ion-Dipole Forces:

\[
\text{Fe}^{2+} + 6 |\text{CN}^- \rightarrow [\text{Fe(CN)}_6]^{4-}
\]

ion - ion

Why not just 5 CN\(^-\)?

\[
3d^6s^0p^0 + 6 \times 2 \rightarrow 3d^{10}4s^24p^6 : 18 \text{ e}^- \text{ Krypton e-configuration}
\]

same with \(\text{Fe(CO)}_5\) but plenty of exceptions to the rule

\[\text{K}_3[\text{Fe(CN)}_6] (17e), [\text{FeCl}_4^-] (13e), \ldots\]

Chemistry of the d-Block Elements

Valence-Bond Theory

Linus Pauling

only individual in history to have won two unshared Nobel Prizes

in Chemistry (1954)
"for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances"

Nobel Peace Price (1962)
Chemistry of the d-Block Elements

Valence-Bond Theory

For a $d^0$ metal ion:

- Inner orbital

For a $d^1$ metal ion:

- Inner orbital

Shortcomings of the Valence-Bond Theory

1) Fails to predict magnetic properties (unpaired electrons)
   e.g.:
   i) all Co(III) Complexes are diamagnetic; except $[\text{CoF}_6]^{3-}$, $[\text{CoF}_3(\text{H}_2\text{O})_3]$
   ii) Cr(III) in $\text{O}_h$: 3 unpaired $e^-\,\text{Cr(II)}$ in $\text{O}_h$: predicted: $2e^-$, exp.: 4 unpaired $e^-$

2) Ni(II) planar vs. octahedral is supposed to introduce change from covalent to ionic
   e.g.: $[\text{Ni(en)}_2]^{2+}$ $2\text{NH}_3 \rightarrow [\text{Ni(NH}_3)_2\text{(en)}_2]$

3) Two Atomic Orbitals (AOs) produce MO$_{\text{bonding}}$ and MO$_{\text{antibonding}}$

4) Color of Transition Metal Complexes! E.g.: $[\text{Ti(\text{H}_2\text{O})}_6]^{3+}$ $\lambda_{\text{max}} = 490$ nm

Chemistry of the d-Block Elements
Chemistry of the d-Block Elements

Crystal Field Theory

Hans Bethe (PhD in theor. physics) 2. Juli 06 – 06. März 05 ;=

Electrostatic Model:

\[ M^+ + L^- \rightarrow [M-L] \]

Underlying Principles:

♦ Ligand-Field Strength
♦ Asymmetric part of the electron interaction
♦ Spin-Orbit Splitting

Chemistry of the d-Block Elements

\( \sigma \) - Symmetrical Metal-Ligand Interaction:

Note Symmetry of Orbitals!

\[ s = g \]
\[ p = u \]
\[ d = g \]
\[ f = u \]

taken from: Harvey & Porter “Introduction to Physical Inorganic Chemistry” Addison-Wesley 1963
Shortcomings of the Crystal-Field Theory

1) Ligands are not negatively charged hard spheres
2) Many complexes with significantly covalent bonds

Chemistry of the d-Block Elements

Molecular Orbital Theory

Friedrich Hund
Chemistry of the d-Block Elements

Molecular Orbital Theory

1) Considers IONIC as well as COVALENT bonding
2) Here: No Mathematical but Phenomenological Considerations
3) MO Theory Contains Aspects of Valence-Bond (VB-) and Crystal-Field Theory

Molecular Orbitals (MOs) are formed via Linear Combination of Atomic Orbitals (AOs)

**metal center**
orbital basis:
5 x \( n \)d - orbitals
1 x \((n+1)s\) - orbital
3 x \((n+1)p\) - orbitals

combines with
ligand
valence orbitals
Can be s, p, or sp\(^n\)
Molecular Orbital Theory

1) Only orbitals with same symmetry interact (e.g.: M=O or M≡O?)

2) For optimal interaction, energy difference should not be too large (e.g.: H-H, H-Cl, NaCl)

3) The better the overlap, the better the orbital combination (see 2. and distance)

Chemistry of the d-Block Elements

not covered in this lecture... try at home!

taken from Riedel „Moderne Anorganische Chemie“ 2. Auflage
MO Theory

MO Diagram for octahedral ($O_h$) $\sigma$-only complexes

How is $\Delta_0$ (in $\sigma$-complexes) explained in terms of MO-Theory?

Chemistry of the d-Block Elements

taken from Cotton, Wilkinson, Gaus „Grundlagen der Anorganischen Chemie“, VCH Verlag
Molecular Orbital Theory

large $\Delta E$ between M and L orbitals
- weak orbital interaction
- small d-splitting (ligand field $\Delta_o$)

small $\Delta E$ between M and L orbitals
- strong orbital interaction
- large d-splitting (ligand field $\Delta_o$)

Chemistry of the d-Block Elements

taken from Cotton, Wilkinson, Gaus „Grundlagen der Anorganischen Chemie“, VCH Verlag
Molecular Orbital Theory

Introduction of metal-ligand \( \pi \)-Interaction:

\[ \begin{align*}
\text{full } \sigma\text{-donor orbital} & \quad \text{empty } \pi\text{-acceptor orbital} \\
\text{full } \sigma\text{-donor orbital} & \quad \text{full } \pi\text{-donor orbital}
\end{align*} \]
### Chemistry of the d-Block Elements

#### Molecular Orbital Theory

**Interpretation of the Spectrochemical Series in Terms of MO Theory**

<table>
<thead>
<tr>
<th>weak ligands</th>
<th>strong ligands</th>
</tr>
</thead>
<tbody>
<tr>
<td>high-spin complexes</td>
<td>low-spin complexes</td>
</tr>
<tr>
<td>strong π-donor</td>
<td>weak π-donor</td>
</tr>
<tr>
<td>pure σ-donor</td>
<td>weak π-acceptor</td>
</tr>
<tr>
<td>strong π-acceptor</td>
<td></td>
</tr>
</tbody>
</table>

\[
\begin{align*}
I^- & < Br^- < S^2^- < SCN^- < Cl^- < NO_3^- < F^- < OH^- < NO_2^- < CN^- < PR_3 < CO \\
H_2O & < NCS^- < CH_3CN < NH_3 < en < bpy < phen \\
\end{align*}
\]

### Chemistry of the d-Block Elements

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
<th>Ligand examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p_\pi - d_\pi )</td>
<td>Donation of electrons from filled ( p )-orbitals of ligand to empty ( d )-orbitals of metal</td>
<td>( RO^-; RS^-; F; Cl^-; R_2N^- )</td>
</tr>
<tr>
<td>( d_\pi - d_\pi )</td>
<td>Donation of electrons from filled ( d )-orbitals of metal to empty ( d )-orbitals of ligand</td>
<td>( R_2S (R_3P, R_3As) )</td>
</tr>
<tr>
<td>( d_\pi - \pi^* )</td>
<td>Donation of electrons from filled ( d )-orbitals of metal to empty ( \pi^* ) (antibonding)-orbitals of ligand</td>
<td>( CO, RNC, pyridine, CN^-; N_2; NO_2^-; ethylene )</td>
</tr>
<tr>
<td>( d_\pi - \sigma^* )</td>
<td>Donation of electrons from filled ( d )-orbitals of metal to empty ( \sigma^* )-orbitals of ligand</td>
<td>( H_2, alkanes )</td>
</tr>
</tbody>
</table>
Molecular - Orbital Diagram for Octahedral Complexes (σ - only)
### Chemistry of the d-Block Elements

<table>
<thead>
<tr>
<th>$C_{1v}$</th>
<th>$E$</th>
<th>$2C_4$</th>
<th>$C_2$</th>
<th>$2\sigma_v$</th>
<th>$2\sigma_d$</th>
<th>$\Delta \eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$R_x$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$R_z$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>$x^2 - y^2$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>$xy$</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>$z, (x, y), (R_x, R_y)$</td>
</tr>
</tbody>
</table>

### Geometry (Symmetry) Dependence of Ligand—Field Splitting (cont'd):

- Octahedral $O_h$
- Axially elongated octahedral $D_{4h}, C_{4v}$
- Square planar $D_{4h}$
- Distorted tetrahedral $D_{2d}$
- Tetrahedral $T_d$

- $\Delta \eta$
- $\Delta T_d$
- $t_2g$
- $e$

- $x^2 - y^2$
- $(x, y)$, $(R_x, R_y)$
- $z^2$
- $x^2 y^2$
- $xy$
- $(xz, yz)$,
A Case Study: The Electronic Structure of Hemoglobin/Myoglobin:

Geometry (Symmetry) Dependence of Ligand—Field Splitting (cont'd):

Observation: Diamagnetic Spin Ground State for the Oxy-Form of Hemoglobin/Myoglobin!

...with Fe$^{III}$ (S = 1/2 or 5/2) and $^3$O$_2$ (S = 1)???
A Case Study: The Electronic Structure of Hemoglobin/Myoglobin:

Observation: Diamagnetic Spin Ground State for the Oxy-Form!
A Case Study: The Electronic Structure of Hemoglobin/Myoglobin:

**Observation:** Diamagnetic Spin Ground State for the Oxy-Form!