Coordination Chemistry I: Structure and Isomers
Synthetic Chemistry

Organic Chemistry

C, O, H, N Chemistry

Inorganic Chemistry

Main group
s, p blocks

Transition metals
d block

Rare earth
f block

Alloys

Thin films

Biological molecules

Catalysts
History of Coordination Chemistry

**Pigments**, such as Prussian blue, copper vitriol...

Fe$_7$(CN)$_{18}$ CuSO$_4$

1798, B. M. Tassaert (France) found that ammonical solutions of cobalt chloride, CoCl$_3$, developed a brownish mahogany color ‘salt’ with composition of CoN$_6$H$_{18}$Cl$_3$ = CoCl$_3$(NH$_3$)$_6$.

, many Co, Ir, Pt compound were prepared, such as CoCl$_3$(NH$_3$)$_6$, CoCl$_3$(NH$_3$)$_5$, CoCl$_3$(NH$_3$)$_4$, CoCl$_3$(NH$_3$)$_3$, PtCl$_4$(NH$_3$)$_2$, ……
Before Werner, chemists defined the valence of an element as the number of its bonds without distinguishing different types of bond.
Ex) Fe: 3, Cl: 1 => FeCl₃  Co: 3
History of Coordination Chemistry

1862, Blomstrand suggested

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>Equivalence of AgCl precipitate (Blomstrand)</th>
<th>Number of ions predicted from conductivity (Werner)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCl₃(NH₃)₆</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>CoCl₃(NH₃)₅</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>CoCl₃(NH₃)₄</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>CoCl₃(NH₃)₄</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>CoCl₃(NH₃)₃</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

1892, Werner considered that the Co-Cl bonds correspond to a "primary" valence of 3 at long distance, while the Co-NH₃ bonds which correspond to a "secondary" or weaker valence (coordination number) of 6 at shorter distance for CoCl₃(NH₃)₆.

\[\text{[Co(NH₃)₆]Cl₃} \quad \text{[Co(NH₃)₅Cl]Cl₂} \quad \text{[Co(NH₃)₄Cl₂]Cl} \quad \text{[Co(NH₃)₃Cl₃]}\]
History of Coordination Chemistry

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCl$_3$(NH$_3$)$_4$</td>
<td>Green</td>
</tr>
<tr>
<td>CoCl$_3$(NH$_3$)$_4$</td>
<td>Violet</td>
</tr>
</tbody>
</table>

Werner further proposed octahedral structures of the cobalt complexes. (‘cause it is the only one to have two isomers out of the other possible six-bonded structures)

Werner-Jørgensen argument: optical isomer of [Co(en)$_2$Cl$_2$]$^+$

Werner: $cis$-[Co(en)$_2$Cl$_2$]$^+$

Jørgensen: coming from C (of other structure)
History of Coordination Chemistry

1914, Werner finally made a optically active complex not-containing C.

And many other achievement, such as

 cis- and trans- Diamminedichloroplatinum(II), [PtCl₂(NH₃)₂]
Definitions

Transition metal complex (Coordination compound)

A metal atom, ion, surrounded by a set of ligands. More specifically (or mostly), a transition metal cation surrounded by neutral molecules or anions with a definite geometry.

Ligand

Any molecule or ion that has at least one electron pair that can be donated to the central metal atom or ion. (can exist independently)

electron donor, Lewis Base, nucleophile (org. term)

electron acceptor, Lewis acid, electrophile (org. term)
Organometallic compound

A transition metal surrounded in part or entirely by organic groups in which a carbon atom is directly bonded to the metal ion.
### Nomenclature

#### monodentate ligands

<table>
<thead>
<tr>
<th>Common Name</th>
<th>IUPAC Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrido</td>
<td>hydrido</td>
<td>$H^-$</td>
</tr>
<tr>
<td>fluoro</td>
<td>fluoro</td>
<td>$F^-$</td>
</tr>
<tr>
<td>chloro</td>
<td>chloro</td>
<td>$Cl^-$</td>
</tr>
<tr>
<td>bromo</td>
<td>bromo</td>
<td>$Br^-$</td>
</tr>
<tr>
<td>iodo</td>
<td>iodo</td>
<td>$I^-$</td>
</tr>
<tr>
<td>nitrido</td>
<td>nitrido</td>
<td>$N^3^-$</td>
</tr>
<tr>
<td>azido</td>
<td>azido</td>
<td>$N_3^-$</td>
</tr>
<tr>
<td>oxo</td>
<td>oxido</td>
<td>$O^{2-}$</td>
</tr>
<tr>
<td>cyano</td>
<td>cyano</td>
<td>$CN^-$</td>
</tr>
<tr>
<td>thiocyano</td>
<td>thiocyano-S (S-bonded)</td>
<td>$SCN^-$</td>
</tr>
<tr>
<td>isothiocyano</td>
<td>thiocyano-N (N-bonded)</td>
<td>$NCS^-$</td>
</tr>
<tr>
<td>hydroxo</td>
<td>hydroxo</td>
<td>$OH^-$</td>
</tr>
<tr>
<td>aqua</td>
<td>aqua</td>
<td>$H_2O$</td>
</tr>
<tr>
<td>carbonyl</td>
<td>carbonyl</td>
<td>$CO$</td>
</tr>
<tr>
<td>thiocarbonyl</td>
<td>thiocarbonyl</td>
<td>$CS$</td>
</tr>
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<td>nitrosyl</td>
<td>nitrosyl</td>
<td>$NO^+$</td>
</tr>
<tr>
<td>nitro</td>
<td>nitrito-N (N-bonded)</td>
<td>$NO_2^-$</td>
</tr>
<tr>
<td>nitrito</td>
<td>nitrito-O (O-bonded)</td>
<td>$ONO^-$</td>
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<td>methyl isocyanide</td>
<td>methylisocyanide</td>
<td>$CH_3NC$</td>
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<tr>
<td>phosphine</td>
<td>phosphane</td>
<td>$PR_3$</td>
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<tr>
<td>pyridine</td>
<td>pyridine (abbrev. py)</td>
<td>$C_5H_5N$</td>
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<td>ammine</td>
<td>ammine</td>
<td>$NH_3$</td>
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<tr>
<td>methylamine</td>
<td>methylamine</td>
<td>$MeNH_2$</td>
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<tr>
<td>amido</td>
<td>azanido</td>
<td>$NH_2^-$</td>
</tr>
<tr>
<td>imido</td>
<td>azanediido</td>
<td>$NH_2^-^-$</td>
</tr>
</tbody>
</table>

### Types of ligand

- monodentate ligands
- ambidentate
# Nomenclature

## Types of ligand

<table>
<thead>
<tr>
<th>Chelating Points</th>
<th>Common Name</th>
<th>IUPAC Name</th>
<th>Abbrev.</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>bidentate</td>
<td>ethylenediamine</td>
<td>1,2-ethanediame</td>
<td>en</td>
<td>NH₂CH₂CH₂NH₂</td>
</tr>
<tr>
<td>tridentate</td>
<td>diethylenetriamine</td>
<td>1,4,7-triazahexane</td>
<td>dien</td>
<td>NH₂CH₂CH₂NHCH₂CH₂NH₂</td>
</tr>
<tr>
<td></td>
<td>1,3,7-triazacyclononane</td>
<td>tacn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetradentate</td>
<td>triethylenetetraamine</td>
<td>1,4,7,10-tetraazadecane</td>
<td>trien</td>
<td>NH₂CH₂CH₂NHCH₂CH₂NHCH₂CH₂NH₂</td>
</tr>
<tr>
<td></td>
<td>β, β’, β”-triaminotriethylamine</td>
<td>β, β’, β”-tris(2-aminoethyl)amine</td>
<td>tren</td>
<td>NH₂CH₂CH₂NCH₂CH₂NH₂</td>
</tr>
<tr>
<td></td>
<td>1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane</td>
<td>TMC</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>tris(2-pyridylmethyl) amine</td>
<td>tris(2-pyridylmethyl) amine</td>
<td>TPA</td>
<td>TPA</td>
</tr>
<tr>
<td>pentadentate</td>
<td>tetraethylene-pentamine</td>
<td>1,4,7,10,13-pentaazatridecan</td>
<td></td>
<td>NH₂CH₂CH₂NHCH₂CH₂NHCH₂CH₂NHCH₂CH₂NH₂</td>
</tr>
<tr>
<td>hexadentate</td>
<td>ethylenediamine-tetraacetate</td>
<td>1,2-ethanediyl (dinitrilo) tetraacetate</td>
<td>EDTA</td>
<td></td>
</tr>
</tbody>
</table>

**multidentate ligands – chelating ligands**

![Ethylenediamine ligand (en)](image)
### Nomenclature Types of ligand

#### Multidentate ligands – chelating ligands

<table>
<thead>
<tr>
<th>Common Name</th>
<th>IUPAC Name</th>
<th>Abbreviation</th>
<th>Formula and Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetylacetonato</td>
<td>2,4-pentanediono</td>
<td>acac</td>
<td>CH$_3$COCHCOCH$_3$</td>
</tr>
<tr>
<td>2,2’-bipyridine</td>
<td>2,2’-bipyridyl</td>
<td>bipy</td>
<td>C$_9$H$_8$N$_2$</td>
</tr>
<tr>
<td>nacac</td>
<td>N,N’-diphenyl-2,4-pentanediamino</td>
<td>nacac</td>
<td>C$<em>{17}$H$</em>{17}$N$_2$</td>
</tr>
<tr>
<td>1,10-phenanthroline</td>
<td>1,10-dianilino</td>
<td>phen, o-phen</td>
<td>C$<em>{12}$H$</em>{12}$N$_2$</td>
</tr>
<tr>
<td>oxalato</td>
<td>oxalato</td>
<td>ox</td>
<td>C$_4$O$_4$^{2-}</td>
</tr>
<tr>
<td>dialkylthiodithiocarbamate</td>
<td>dialkylthiocarbamate</td>
<td>dic</td>
<td>S$_2$CR$_2$^-</td>
</tr>
<tr>
<td>ethylenedithiolate</td>
<td>1,2-ethanediol</td>
<td>dithiolene</td>
<td>S$_2$C$_2$H$_4$^-</td>
</tr>
<tr>
<td>1,2-bis(diphenylphosphino)</td>
<td>1,2-ethanediphosphino</td>
<td>dpp</td>
<td>Ph$_2$PC$_2$H$_4$PPh$_2$</td>
</tr>
<tr>
<td>BINAP</td>
<td>2,2’-bis(diphenylphosphino)</td>
<td>BINAP</td>
<td>Ph$_3$P(C$_6$H$_4$)$_2$PPh$_2$</td>
</tr>
<tr>
<td>dimethylglyoximato</td>
<td>butanedione</td>
<td>DMG</td>
<td>HONCC(CH$_3$)$_2$(CH$_3$)NO^-</td>
</tr>
<tr>
<td>pyrazolylborato (scorpionate)</td>
<td>hydrotris(pyrrozolyl)borato</td>
<td>Tp</td>
<td>[HBI(C$_3$H$_3$N$_2$)$_3$]^-</td>
</tr>
<tr>
<td>salen</td>
<td>2,2’-Ethylendiole</td>
<td>salen</td>
<td>OP$_2$(CHNCH$_2$CH$_2$NC$\text{H}_3$)PHO^-</td>
</tr>
</tbody>
</table>

![Diagram of a complex with Cu and ligands](image1.png)

![Diagram of a molecular structure](image2.png)
Nomenclature

1. The cation comes first, followed by anion. (same as in salts)
   Ex) \([\text{Ag(NH}_3\text{)}_2]\text{Cl} = \text{diamminesilver(I) chloride}\)
   \(\text{K}_3[\text{Fe(CN)}_6] = \text{potassium hexacyanoferrate(III)}\)

2. Inner sphere complex ion is enclosed in square brackets in the formula.
   In the nomenclatures,
   the ligands are named before the metal within the coordination sphere.
   a space only between cation and anion.
   In the formulas, the metal comes first.
   Ex) \([\text{Cu(NH}_3\text{)}_4]\text{SO}_4 = \text{tetraamminecopper(II) sulfate}\)
   \([\text{Co(NH}_3\text{)}_6]\text{Cl}_3 = \text{hexaamminecobalt(III) chloride}\)

3. Prefixes are used for the number of ligands of one kind. If the ligand name contains the prefixes or is complicated, -is type prefixes are used.
   Ex) \([\text{Co(en)}_2\text{Cl}_2]\text{F} = \text{dichlorobis(ethylenediamine)cobalt(III) fluoride}\)
   \([\text{Fe(bipy)}_3]\text{Cl}_2 = \text{tris(bipyridine)iron(II) chloride}\)

<table>
<thead>
<tr>
<th>Number</th>
<th>Prefix</th>
<th>-is Type Prefix</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>di</td>
<td>bis</td>
</tr>
<tr>
<td>3</td>
<td>tri</td>
<td>tris</td>
</tr>
<tr>
<td>4</td>
<td>tetra</td>
<td>terakis</td>
</tr>
<tr>
<td>5</td>
<td>penta</td>
<td>pentakis</td>
</tr>
<tr>
<td>6</td>
<td>hexa</td>
<td>hexakis</td>
</tr>
<tr>
<td>7</td>
<td>hepta</td>
<td>heptakis</td>
</tr>
<tr>
<td>8</td>
<td>octa</td>
<td>octakis</td>
</tr>
<tr>
<td>9</td>
<td>nona</td>
<td>nonakis</td>
</tr>
<tr>
<td>10</td>
<td>deca</td>
<td>decakis</td>
</tr>
</tbody>
</table>
4. Ligands are named in alphabetical order (not the prefixe).

Ex) \([\text{Co(NH}_3\text{)}_4\text{Cl}_2]^+ = \text{tetraamminedichlorocobalt(III)}\)

\([\text{Pt(NH}_3\text{)}\text{BrCl(CH}_3\text{NH}_2\text{)}] = \text{amminebromochloromethylamineplatinum(II)}\)

5. Ligand naming:

Ex) Anionic ligands are given an \(\text{o}\) suffix: chloro, fluoro, oxo, sulfato

Neutral ligands retain their usual name: methylamine, bipyridine

Water: aqua, \(\text{NH}_3\): ammine (distinguishes from alkylamines)

6. Two systems for designating charge or oxidation number:

(a) Stock system: puts oxidation number of the metal ion in Roman numerals in parenthesis after the name of the metal ion. (more common)

(b) Ewing-Basset system: puts the charge of the total complex ion in parenthesis after the name of the metal ion.

(c) \(\text{ate}\) to the metal name if the complex ion has an overall (-) charge

Ex) \([\text{Pt(NH}_3\text{)}_4]^2+ = \text{tetraammineplatinum(II)} \text{ or tetraammineplatinum(2+)}\)

\([\text{PtCl}_4]^{2-} = \text{tetrachloroplatinate(II)} \text{ or tetrachloroplatinate(2-)}\)

\([\text{PtCl}_6]^{2-} = \text{hexachloroplatinate(IV)} \text{ or hexachloroplatinate(2-)}\)
Nomenclature

7. *cis-* , *trans-* (and other prefix for isomers) before the nomenclature in *italics*.

Ex) *cis*-diamminedichloroplatinum(II)

*trans*-diamminedichloroplatinum(II)

8. Bridging ligands have the prefix of µ

Ex) \[(\text{NH}_3)_4\text{Co(OH)(NH}_2\text{)Co(NH}_3)_4]\text{]^4+} = \text{µ-amido-µ-hydroxobis(tetraaminecobalt)(III)}

\[[\text{Co(Co(NH}_3)_4(\text{OH})_2)_3]\text{]^6+} = \text{tris(tetraammine-µ-di hydroxocobalt)cobalt(6+)}

9. Negatively charged complexes of certain metals use their Latin names:

Fe (iron) = ferrate  \[\text{FeCl}_4^-\]  = tetrachloroferrate(III) or tetrachloroferrate(1-)

Ag (silver) = argenate  \[\text{Au(CN)}_2^-\]  = dicyanoaurate(I) or dicyanoaurate (1-)

Pb (lead) = plumbate  Sn (tin) = stannate  Sb (antimony) = stibate  Au (gold) = aurate
Isomerism

Stereo Isomers (identical bonds)

Are the bonds between the same atoms?

Yes

Stereo or configurational isomers

Is each identical to its mirror image?

Yes

Diastereomers or geometric isomers

May have conformational isomers (different twists or bends of bonds)

No

Enantiomers or optical isomers

Chiral, nonsuperimposable mirror images

Structural Isomers (different bonds)

No

Structural or constitutional isomers

Ionization isomers

Linkage isomers

Coordination isomers

Hydrate isomers
Isomerism

Constitutional Isomers (Structural Isomers)

Hydrate isomerism: having water as either a ligand or an added part of the crystal structure
**Isomerism**

**Constitutional Isomers (Structural Isomers)**

**Ionization isomerism**: exchange of ions inside and outside coordination sphere

\[
\text{Br}^{-} \quad \text{NH}_{3} \quad \text{NH}_{3} \quad \text{NH}_{3} \quad \text{NH}_{3} \quad \text{Co}^{2+} \quad \text{SO}_{4}^{2-} \quad \text{NH}_{3} \quad \text{NH}_{3} \quad \text{NH}_{3} \quad \text{Br}^{-}
\]

\[
[\text{Co(NH}_{3}\text{)}_{4}(\text{H}_{2}\text{O})\text{Cl}]\text{Br}_{2} \text{ and } [\text{Co(NH}_{3}\text{)}_{4}\text{Br}_{2}]\text{Cl}\cdot\text{H}_{2}\text{O}
\]

\[
[\text{Co(NH}_{3}\text{)}_{5}\text{SO}_{4}]\text{NO}_{3} \text{ and } [\text{Co(NH}_{3}\text{)}_{5}\text{NO}_{3}]\text{SO}_{4}
\]

**Coordination isomerism**: occurs in compound containing both anion and cation complexes

\[
[\text{Co(en)}_{3}]^{3+}[\text{Cr(CN)}_{6}]^{3-} \quad [\text{Pt(NH}_{3}\text{)}_{4}]^{2+}[\text{PtCl}_{6}]^{2-}
\]

\[
[\text{Cr(en)}_{3}]^{3+}[\text{Co(CN)}_{6}]^{3-} \quad [\text{Pt(NH}_{3}\text{)}_{4}\text{Cl}_{2}]^{2+}[\text{PtCl}_{4}]^{2-}
\]
Isomerism

Constitutional Isomers (Structural Isomers)

Linkage (ambidentate) isomerism: occurs in compounds containing ambidentate ligands

Intramolecular rearrangement (kinetic and $^{18}$O labeling expmt)

$$\text{[O} - \text{N} - \text{Ru(NO)}_4(\text{OH})\text{]}^{2-} \rightleftharpoons \text{[N} - \text{O} - \text{Ru(NO)}_4(\text{OH})\text{]}^{2-}$$

Stable form

Metastable form
**Isomerism**

**Optical isomerism**: when mirror image is nonsuperimposable

**Geometrical isomerism**: stereoisomerism except for the optical isomerism

Chiral complex: complex not superimposable on its own mirror image

Optically active: rotating the plane-polarized light

Enantiomers: mirror-image partners

Molecules with $S_n \not\rightarrow$ no chirality ($i = S_2, \sigma = S_1$)
Isomerism

Stereoisomers

CN=4

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

\[\text{[PtBrCl(PR_3)_2]}\]

\[\text{^{31}P NMR} \quad 1 \text{ peak}
\]

\[\text{^{31}P NMR} \quad 2 \text{ peaks}
\]

CN=6

\[\text{MX}_4\text{Y}_2\]

\[\text{cis} : \text{NH}_3 & \text{Cl} & \text{NH}_3 & \text{Cl} & \text{NH}_3 \\
\text{trans} & : \text{NH}_3 & \text{Cl} & \text{NH}_3 & \text{Cl}
\]

\[\text{[Co(NH}_3)_3\text{Cl}_3]\]

\[\text{[Co(dien)_2]}^{3+}\]

\[\text{MX}_3\text{Y}_3\]

\[\text{fac (facial)}
\]

\[\text{mer (meridional)}
\]

\[\text{fac (facial)}
\]

\[\text{mer (meridional)}
\]
Isomerism

CN=6 (cont’d)

enantiomer pair

\[ \text{No coplanar rings} \]
\[ \text{Two coplanar rings} \]
\[ \text{Three coplanar rings} \]

many other geometrical isomers….
Isomerism

CN=6 (cont’d)  Isomers of Mabcdef (O₈)

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
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<td>ab</td>
<td>ab</td>
</tr>
<tr>
<td></td>
<td>cd</td>
<td>ce</td>
<td>cf</td>
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<tr>
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<td>ef</td>
<td>df</td>
<td>de</td>
</tr>
<tr>
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<td>ac</td>
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<td>bf</td>
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<td>bf</td>
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<td>ce</td>
<td>cd</td>
</tr>
</tbody>
</table>

Total = 30

NOTE: *Each 1x3 box is a set of three trans pairs of ligands. For example, box C3 represents the two enantiomers of [M < ad > < bf > < ce >].
Isomerism

CN=6 (cont’d) Isomers of Ma\textsubscript{2}bcde (O\textsubscript{h})

15 stereoisomers (6 pairs of enantiomers)
<table>
<thead>
<tr>
<th>Formula</th>
<th>Number of Stereoisomers</th>
<th>Pairs of Enantiomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ma_6</td>
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<tr>
<td>Ma_5b</td>
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<tr>
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<td>15</td>
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<tr>
<td>M(AB)(AB)cde</td>
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<tr>
<td>M(AB)(AB)cd</td>
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<tr>
<td>M(AB)(CD)e_f</td>
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<tr>
<td>M(AB)_3</td>
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<td>2</td>
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<tr>
<td>M(ABA)cde</td>
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<td>M(ABC)_2</td>
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<td>5</td>
</tr>
<tr>
<td>M(ABBA)cd</td>
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<td>3</td>
</tr>
<tr>
<td>M(ABCBA)d</td>
<td>7</td>
<td>3</td>
</tr>
</tbody>
</table>

**NOTE:** Uppercase letters represent chelating ligands, and lowercase letters represent monodentate ligands.
Isomerism

Optical isomers of octahedral complexes with chelate rings ($\Lambda$, $\Delta$)

Handedness

$\Lambda$ Isomers

$\Delta$ Isomers
Optical isomers of octahedral complexes with chelate rings ($\Lambda$, $\Delta$)

Procedure to determine handedness

Isomerism
Isomerism

Optical isomers of octahedral complexes with chelate rings (Λ, Δ)

Co(EDTA)−

ΛΔΛ-(ethylenediaminotetraacetato)cobaltate(III)
= ΛΛΔ-
= ΔΛΛ-
Isomerism

Optical isomers of octahedral complexes with chelate rings ($\Lambda$, $\Delta$)

Co(EDTA)$^-$

$\Lambda\Delta\Delta$-(ethylenediaminetetraacetato)cobaltate(III)

$= \Delta\Lambda\Delta$- "

$= \Delta\Delta\Lambda$- "

Stereoisomers
Isomerism

Optical isomerism arising from ligand ring conformation ($\lambda$, $\delta$)

Many chelate rings are not planar, they can have different conformations in different molecules.

Ex) ethylenediamine (en):
1st line – connecting atoms bonded to the metal
2nd line – connecting two carbon atoms

rotation of the 2nd line: counterclockwise $\rightarrow \lambda$
rotation of the 2nd line: clockwise $\rightarrow \delta$

Ex) $[\text{Co}(en)_3]^{3+}$ $\Lambda\lambda\lambda-\text{[Co(en)$_3$]}^{3+}$ is more stable than $\Delta\delta\delta\delta-\text{[Co(en)$_3$]}^{3+}$ in calculation
$\Lambda\delta\delta\delta-\text{[Co(en)$_3$]}^{3+}$ is more stable than $\Lambda\lambda\lambda-\text{[Co(en)$_3$]}^{3+}$ in calculation

actually, in solution $\lambda \leftrightarrow \delta$ interconversion
in soln, $\delta\delta\lambda$ is most abundant in $\Lambda$ form
Optical isomerism arising from ligand ring conformation ($\lambda$, $\delta$)

Chiral structures of $\text{trans-}[\text{CoX}_2(\text{trien})]^+$

only 1 choice of $\lambda$

$\delta\delta$

$\delta\lambda$

$\lambda\lambda$
Isomerism

Optical isomerism arising from the chiral center of ligands (R, S)

Cahn-Ingold-Prelog Rules

Ligand precedence rules

1. Ligands of the higher atomic number precede those with lower ones, e.g. Br precedes Cl (Br>Cl).

2. For ligands with the same type of atoms linked to the center C, the precedence is determined based on the atomic numbers of ligands in the next sphere, e.g. ligand with C-O sequence precedes C-C. If no difference is detected, the determination is based on the distinction in the next spheres, and search is continued until the difference is detected.

3. The coordination number of non-hydrogen atoms is assumed to be 4, i.e. atoms bonded with multiple bonds are considered to be bonded to multiple atoms, e.g. carbonyl carbon is treated as if it was bonded to two oxygen atoms, and carboxyl carbon as if it was bonded to three oxygens (these are then called phantom atoms). Ligand duplication is also necessary in the cases of cyclic systems.

4. Ligands of the same atomic number, but a higher atomic mass precede those with a lower atomic mass, e.g. D precedes H (D>H). This criterion applies only after the previous ones were exhausted.

5. For compounds where only configurational (not constitutional) differences between ligands are detected, the following rules apply:  
   a. The olefinic ligand that has the chiral center and another ligand on the same side of the double bond (cis) precedes the one with the trans-configuration.  
   b. Ligands with R,R or S,S precede R,S or S,R.  
   c. R precedes S.
Isomerism

Ex) [CoX₂(trien)]⁺

geometrical

α β

optical
(chirality on chelate-ring conformation)

Λ Δ Λ Δ

optical
(chirality on ligands)

RR SS SS RR
Isomerism

Separation and Identification of Isomers

**Separation**

1. **Geometric isomers** can be separated by fractional crystallization with different counterions. -
   - Due to the slightly different shapes of the isomers.
   - The ‘fit’ of the counterion can greatly influence solubility.
   - Solubility is the lowest when the positive and negative charges have the same size and magnitude of charges (Basolo).

2. **Optical isomers**: Separations are performed with chiral counterions.
   - The resulting physical properties will differ allowing separation.
Isomerism

Separation and Identification of Isomers

Identification of optical isomers (CD and ORD)

Plane-polarized light
= right circularly polarized light
+ left circularly polarized light

http://www.enzim.hu/~szia/cddemo/edemo0.htm
Circular dichroism (CD) is the absorption difference between left and right circularly polarized light at a given wavelength. => absorptive

Circular dichroism = \( \varepsilon_l - \varepsilon_r \)

\( \varepsilon_l \neq \varepsilon_r, \ n_l = n_r \)
Identification of optical isomers (CD and ORD)

Optical rotatory dispersion (ORD): The variation of optical rotation as a function of wavelength. (Cotton effect for a single band) => dispersive

$$\alpha = \frac{n_l - n_r}{\lambda}$$

Cotton effect: In a wavelength region where the light is absorbed, the absolute magnitude of the optical rotation at first varies rapidly with wavelength, crosses zero at absorption maxima and then again varies rapidly with wavelength but in opposite direction.

$$\mathcal{C}_l \neq \mathcal{C}_r, \; n_l \neq n_r \; \text{(Almost all the chiral molecules)}$$
Isomerism

Separation and Identification of Isomers

Identification of optical isomers (CD and ORD)

- CD: 
  - $\Delta \varepsilon$
  - $\alpha$

- ORD: 
  - $\alpha$
  - $\Delta \varepsilon$

UV/Vis

Magnitude of rotation (ORD) or ellipticity (CD)

Enantiomer of A
Isomerism

Identification of optical isomers (CD and ORD)

- **Dextrorotation** (d- or (+)-): rotating plane polarized light clockwise
- **Levorotation** (l- or (-)-): counterclockwise
K: 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\)4s\(^1\) = [Ar]4s\(^1\)
Ca: [Ar]4s\(^2\)
Sc: [Ar]4s\(^2\)3d\(^1\)
Ti: [Ar]4s\(^2\)3d\(^2\)

Cations
K\(^+\): [Ar]
Ca\(^+\): [Ar]4s\(^1\)

V\(^{2+}\): [Ar]3d\(^3\)
Cr\(^{2+}\): [Ar]3d\(^4\)
Mn\(^{2+}\): [Ar]3d\(^5\)
Fe\(^{2+}\): [Ar]3d\(^6\)
Co\(^{2+}\): [Ar]3d\(^7\)
Ni\(^{2+}\): [Ar]3d\(^8\)
Cu\(^{2+}\): [Ar]3d\(^9\)
Zn\(^{2+}\): [Ar]3d\(^{10}\)

always s electrons are out first.

transition metals
## Coordination Numbers and Structures

Two most important concepts in transition-metal complex chemistry

### Oxidation states of metals

<table>
<thead>
<tr>
<th></th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
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</tbody>
</table>

O : most common
Coordination Numbers and Structures

Two most important concepts in transition-metal complex chemistry

Oxidation states of metals

Factors

1. Number of bonds
2. VSEPR arguments
3. Occupancy of d-orbitals (LFT)
4. Steric inference by large ligands
5. Crystal packing effects

Coordination numbers and geometries

<table>
<thead>
<tr>
<th>CN</th>
<th>Geometries</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>rare</td>
</tr>
<tr>
<td>2</td>
<td>Linear (rare)</td>
</tr>
<tr>
<td>3</td>
<td>Trigonal-plane</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedron, Square-plane</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramid, Square pyramid</td>
</tr>
<tr>
<td>6</td>
<td>Octahedron, Triogonal prism</td>
</tr>
<tr>
<td>7</td>
<td>Pentagonal bipyramid, Capped trigonal prism, Capped octahedron</td>
</tr>
<tr>
<td>8≤</td>
<td>Known up to 16 CN</td>
</tr>
</tbody>
</table>
Coordination Numbers and Structures

**CN = 1** : very rare

- Tl(I): sterically hindered
- VO$^{2+}$: as a transient species

**CN = 2** : rare, linear ($D_{\infty h}$)

- Mostly d$^{10}$ compounds
  - $H_3N \cdash Ag \cdash NH_3^+$
  - $Cl \cdash Cu \cdash Cl^-$
  - NC $\cdash$ Hg $\cdash$ CN
  - CN $\cdash$ Au $\cdash$ CN$^-$

None d$^{10}$ complexes also exist.
- Ex) Mn(II) with bulky ligands

\[ [\text{Mn(N(SiMePh$_2$)$_2$)$_2$}] \]
Coordination Numbers and Structures

CN = 3: rare, trigonal plane (D₃h)

HgI₃⁻ (d¹⁰)

Complexes with bulky ligands
Coordination Numbers and Structures

$CN = 4$: tetrahedron ($T_d$), square plane ($D_{4h}$)

$T_d$: very common

$D_{4h}$: $d^8$ such as Ni(II), Pt(II), Pd(II)

and others

(T$_d$ at 75$^\circ$C)

at 25$^\circ$C
Coordination Numbers and Structures

CN = 4 : tetrahedron (T_d), square plane (D_{4h})

\[
\text{[NiBr}_2(\text{P(C}_6\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_5)))_2] : \text{both T}_d \text{ and D}_{4h} \text{ in the same crystal}
\]

\[
\text{[Ni(PR}_3)_2X_2]
\]

\[
\text{(T}_d \text{ at 75}^\circ\text{C)}
\]

\[
\text{at 25}^\circ\text{C}
\]

\[\Delta E \text{ is not big}\]
Coordination Numbers and Structures

CN = 5: trigonal bipyramid ($D_{3h}$), square pyramid ($C_{4v}$)

$D_{3h}$ and $C_{4h}$ coexist in crystal

V(IV): $d^1$

V(V): $d^0$
Coordination Numbers and Structures

**CN = 5**: trigonal bipyramid ($D_{3h}$), square pyramid ($C_{4v}$)

Fe(CO)$_5$

Crystal: 180.6 pm

CO

183.3 pm

Fluxional behavior (Berry pseudorotation)

$\Delta E$ between $D_{3h}$ and $C_{4v}$ is very small.

$^{13}$C NMR in solution

(a) (b) (c)
Coordination Numbers and Structures

**CN = 6**: octahedron \((O_h)\)

- **octahedron** \((O_h)\): very common
- **variations of** \(O_h\)
  - tetragonal elongation
  - ex) Cu(II) : \(d^9\)
  - tetragonal compression
  - ex) Ti(III) : \(d^1\)
- **D_{4h}**

**variations of** \(O_h\)

- trigonal elongation
  - : trigonal antiprism \((D_{3d})\)
- and 60° rotation
  - : trigonal prism \((D_{3h})\)
- usually with three bidentate ligands
Coordination Numbers and Structures

CN = 7: pentagonal bipyramid ($D_{5h}$)
capped trigonal prism, capped octahedron
Coordination Numbers and Structures

CN ≥ 8
Ligand can act as bridges to create more extended structures.

**Zeolites** are microporous, aluminosilicate, minerals commonly used as commercial adsorbents.

**Metal-Organic Frameworks (MOFs)** are crystalline compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one-, two-, or three-dimensional structures that can be porous.

ligand “building block”
Coordination Frameworks

Metal-Organic Polyhedron

m-BDC

Many other MOFs
Multimetallic Complexes

metal clusters: with direct M-M bonds  (in real world, metal cluster is more common for both)
cage complexes: without direct M-M bonds

Metal-sulfur clusters in Nitrogenase

\[
\text{N}_2 + 8\text{H}^+ + 8\text{e}^- + 16\text{MgATP} \rightarrow 2\text{NH}_3 + \text{H}_2 + \text{Pi} + 16\text{MgATP}
\]