Isomerism in Coordination Chemistry
(Chapter 20 H&S)

Isomers
Compounds with same formula but different atom arrangement

Structural Isomers
Compounds with different connections between atoms

- Linkage isomers
  Same ligand connected by different atoms

- Ionization isomers
  Give different ions in solution

Polymerization isomers
Same empirical formula but different molar mass

Coordination isomers
Different ligand sets in complex cation and anion

Hydration isomers
Contain different numbers of waters inner/outer sphere

Stereoisomers
Compounds with same connectivity but different spatial arrangement

- Diastereomers (Geometric isomers)
  Non-mirror images OR different coordination polyhedra

- Optical isomers (Enantiomers)
  Mirror image isomers
Structural Isomerism

**Linkage isomers:** same ligand connected by different atoms

*eg.* thiocyanate $\text{SCN}^-$ contains two donors: N or S

$[\text{Co(NH}_3)_5\text{(NCS-S)}]^2^+ \text{ and } [\text{Co(NH}_3)_5\text{(NCS-N)}]^2^+$

Formal ox. st.? $d^n$ count? $\text{Co}^{3+} \quad d^6$

**Ionization isomers:** different ions when dissolved

exchange of ions between inner and outer coordination sphere

*eg.* $[\text{Co(NH}_3)_5\text{Br}]\text{[SO}_4\text{]}$ vs. $[\text{Co(NH}_3)_5\text{(SO}_4\text{)}]\text{Br}$

Methods to distinguish these?

1) wet chemistry: precipitate 'free' ions

$\text{[Co(NH}_3)_5\text{Br]}\text{[SO}_4\text{]} \xrightarrow{\text{Ba(NO}_3\text{)}_2\text{ (aq)}} \text{BaSO}_4\text{ (s)} \quad \text{[Co(NH}_3)_5\text{Br]}\text{[NO}_3\text{]}_2\text{ (aq)}$

$\text{[Co(NH}_3)_5\text{(SO}_4\text{)}]\text{Br} \xrightarrow{\text{AgNO}_3\text{ (aq)}} \text{AgBr (s)} \quad \text{[Co(NH}_3)_5\text{(SO}_4\text{)}]\text{[NO}_3\text{]}\text{ (aq)}$

2) IR spectroscopy

free $\text{SO}_4^{2-}$

bound $\text{SO}_4^{2-}$

one SO stretch

three SO stretches
Polymerization isomers: identical empirical formulae but different molar masses (i.e. different degrees of aggregation)

\[
[R_2\text{Al}(\text{CN})]_3 \quad \text{and} \quad [R_2\text{Al}(\text{CN})]_n \quad (n>6)
\]

Coordination isomers: found in special cases where both the cation and anion are complexes

egs. \[\text{[Co(NH}_3\text{)}_6][\text{Cr(CN)}_6]\] vs. \[\text{[Cr(NH}_3\text{)}_6][\text{Co(CN)}_6]\]

\[\text{[Pt(NH}_3\text{)}_4][\text{PtCl}_6]\] vs. \[\text{[Pt(NH}_3\text{)}_6\text{Cl}_2][\text{PtCl}_4]\]

What are the formal charges and \(d^n\) configurations here?
Co and Cr are 3+: \(\text{Cr}^{3+} \quad d^3\) and \(\text{Co}^{3+} \quad d^6\)
Pt\(^{4+}\) (octahedral) and Pt\(^{2+}\) (sq. planar): \(\text{Pt}^{4+} \quad d^6\) and \(\text{Pt}^{2+} \quad d^8\)

Hydration isomers: exchange of water and another ligand between inner and outer coordination sphere

eg. \[\text{[Cr(H}_2\text{O})_4\text{Cl}_2]\text{Cl}\cdot2\text{H}_2\text{O}\] (green crystals from c. HCl soln)

\[\rightarrow\text{(dissolve } \text{H}_2\text{O}) \quad \text{[Cr(H}_2\text{O})_5\text{Cl}]\text{Cl}_2\cdot\text{H}_2\text{O} \quad \text{(blue-green)}\]

\[\rightarrow\text{(heat)} \quad \text{[Cr(H}_2\text{O})_6]\text{Cl}_3 \quad \text{(violet)}\]

How can you tell the difference? Colour (UV/Vis) Ag\(^+\) precipitation
Stereoisomerism

Diastereoisomers (geometrical isomers): essentially includes all isomers that have the same M-L connectivity but a different spatial arrangement of donors AND are not mirror image isomers

Note: this wider definition includes what are often termed ‘geometrical’ isomers such as cis/trans complex and complexes of different polyhedral arrangements (eg. sq. pyramidal vs. TBP). While strictly correct, some prefer to reserve the term ‘diastereomers’ for optical isomers that are NOT enantiomers (i.e. in the same way it is used in organic chemistry: eg. RR and RS are diastereomers but not enantiomers)

CN 4

Square planar: ML₂X₂ type

cis and trans isomers

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

cis-platin was the original Pt based chemotherapy drug (interferes with DNA)

not as easy to make as it looks (more on this later...)
CN 5  (isomers defined below often interconvert)

**TBP:**  MXL$_4$ and MX$_2$L$_3$

![Diagram of MXL$_4$ and MX$_2$L$_3$ isomers]

**SqPyr:**  MXL$_4$ and MX$_2$L$_3$

![Diagram of MXL$_4$ and MX$_2$L$_3$ isomers]
**CN 6**

*Oh*: all vertices identical so only one structure for MXL₅

- **MX₂L₄**
  - *trans*: replace any L with X
  - *cis*: replace any L trans to X with X

- **MX₃L₃**
  - Meridional
  - **mer**
  - Facial
  - **fac**

- **Only mer**
- **Only fac**
Optical isomers (enantiomers): only includes isomers that are optically active (rotate plane-polarized light) and mirror images

Special case in Oh metal complexes: helical chirality of tris(chelates)

e.g. Co(acac)_3