Lecture 6 - Chirality in Inorganic Chemistry and Isomers of 4-Coordinate Metal ions

- Review of chirality in inorganic chemistry.
- Geometric and stereoisomers of tetrahedral and square planar complexes.
- What should a bonding theory explain? - colors of transition metal complexes

1. Chirality in Inorganic Chemistry

The Rule

- A molecule is chiral if it is **non-superimposable** on its mirror image.
- In almost all cases, a chiral molecule lacks a plane of symmetry (mirror plane) $\sigma$ and an inversion centre, $i$.

Example - Reflection through a plane of symmetry (mirror plane).

- There is a mirror plane that bisects the molecule. The carbon atoms symmetrically disposed across the mirror plane are equivalent.

**meta-xylene** - a disubstituted benzene ring.

Chiral molecules have no mirror planes.
Example - Reflection through an inversion centre (centre of symmetry)

- If you can pass each part of a molecule through a point in the center and the resulting structure is identical to the original structure, the molecule has an inversion center, \( i \).
- The operation of passing the parts of a molecule through such a center is the operation of inversion.
- Imagine a point at the center of the \( C_4 \) ring. This is the inversion center. All atoms can pass straight through this point to equivalent positions on the other side of the molecule. The fluorine atoms are equivalent because of this inversion.

\[ \text{trans-difluorocyclobutane.} \]

Chiral molecules have no inversion centers.

- Human hands are perhaps the most universally-recognized example of chirality: The left hand is a non-superimposable mirror image of the right hand; no matter how the two hands are oriented, it is impossible for all the major features of both hands to coincide.
- A helical chain such as DNA or a "heltaskelta" slide are chiral compounds/objects.
- If a clockwise movement of the helix corresponds to axial movement away from the observer, then it is a right-handed helix.
- If counter-clockwise movement corresponds to axial movement away from the observer, it is a left-handed helix.
- Handedness or chirality is a property of the helix: a right-handed helix cannot be turned or flipped to look like a left-handed one unless it is viewed through a mirror, and vice versa.

\[ \text{A natural left-handed (counterclockwise) helix, used by a climber plant.} \]
Chirality and Art. - M. C. Escher’s "Bond of Union": the woman’s head is a left-handed helix whilst the man’s head is a right-handed helix.

Chirality is also found in propellers, spiral staircases and pasta spirals etc..

Chirality in Octahedral Complexes

Six coordinate complexes in which there are three bidentate ligands e.g. (en), (ox), (acac) possess non-superimposable mirror images.
This type of chirality is often referred to as "Propeller Chirality".

A right-handed (clockwise) twist of a propeller cannot be turned or flipped to look like a left-handed (anticlockwise) propeller unless it is viewed through a mirror, and vice versa.

Propeller Chirality

\[ \Lambda \text{ (left-handed twist)} \]
\[ \Lambda \cdot [\text{Fe(ox)}_3]^{3-} \]
\[ \Delta \text{ (right-handed twist)} \]
\[ \Delta \cdot [\text{Fe(ox)}_3]^{3-} \]

The Fe ion may be regarded as a stereogenic center. The two enantiomers of complexes such as \([\text{Fe(ox)}_3]^{3-}\) may be designated as \(\Lambda\) (left-handed twist of the propeller described by the ligands) and \(\Delta\) (right-handed twist).
2. Geometric and Optical Isomerism for some Tetrahedral and Square Planar Metal Complexes

In the following examples we will contrast the number and types of isomers for tetrahedral vs. square planar complexes with a particular composition. The different number and kinds of isomers obtained for a given composition allowed a determination of geometry in the days before X-ray crystallography and other modern techniques were available to researchers.

1. Tetrahedral $MA_2B$ has no isomers, but square planar $MA_2B_2$ has geometric isomers.

Four-coordinate platinum(II) complexes are always square planar, whereas 4-coordinate cobalt(II) complexes are tetrahedral. The cis and trans isomers of diammine-dichloroplatinum(II) are shown below.

On the other hand, tetrahedral diamminedichlorocobalt(II) has no isomers, either geometric or optical. (As you would expect, given your familiarity with such carbon compounds as $CH_2Cl_2$).

2. Tetrahedral $MABCD$ has optical isomers but not geometric isomers; square planar $MABCD$ has geometric isomers but not optical isomers. In the sketch below, $M$ can be any metal that exhibits square planar coordination. The three isomers place $A$ trans to $C$, $A$ trans to $B$, and $A$ trans to $D$.

None of these is chiral (the square plane is the plane of symmetry in these complexes).
Tetrahedral MABCD is analogous to carbon bonded to four different groups, and thus has **optical isomers**, but not geometric isomers.

Remember from Lecture 5, the $[\text{Co(NH}_3\text{)}\text{ClBrI}]^-$ ion is tetrahedral, with four different groups bonded to the cobalt, and has two non superimposable mirror images:

$$\text{[Co(NH}_3\text{)}\text{ClBrI}]^-$$

3. Neither tetrahedral $M(A-A)_2$ nor square planar $M(A-A)_2$ have isomers, as long as the chelating ligands are symmetrical and there are no chiral centers on the ligands.

For example $M(\text{en})_2$  
$\text{en = H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$

Remember **cis only coordination** for en, never trans

No geometric isomers and no optical isomers because it has internal mirror planes of symmetry e.g.

$$\text{plane of symmetry - the front half looks like the back half}$$

Remember that any object that has an **internal mirror plane of symmetry cannot be chiral**, i.e. it does not have optical isomers

For $M(\text{en})_2$

Tetrahedral Metal ion - No geometric isomers, No optical isomers  
Square planar Metal ion - No geometric isomers, No optical isomers
4. **Tetrahedral** \(M(A-B)_2\) **has optical isomers but not geometric isomers; square planar** \(M(A-B)_2\) **has geometric isomers but not optical isomers.**

- Real examples of unsymmetrical \(A-B\) ligands are *aminoethanethiolate* and *benzoylacetonate* complexes. Aminoethanethiolate is \(\text{NH}_2\text{CH}_2\text{CH}_2\text{S}^-\)

  ![Resonance structures for benzoylacetonate](image)

- Consider the aminoethanethiolate complexes of square planar platinum(II) and tetrahedral cobalt(II).

  ![Geometric isomers of \([\text{Pt(NH}_2\text{CH}_2\text{CH}_2\text{S})_2]\)](image)

  **Square planar - geometrical isomers (cis and trans) no enantiomers, i.e. no optical isomers.**

  ![Optical isomers of \([\text{Co(NH}_2\text{CH}_2\text{CH}_2\text{S})_2]\)](image)

  **No geometric isomers. Optical isomers - use your model kits to build them, you will see that you cannot superimpose them, they have a "screw sense" i.e. they are left or right handed.**

**Problem:** The following pairs of Co coordination complexes are isomers:
1. (a) 1. (b)
2. (a) 2. (b)
3. What Should a Bonding Theory Explain?

We will look at some of the properties of transition metal complexes that we want a bonding theory to address. We will ask questions about the varying behaviors and properties of different complexes that are not explainable by bonding theories such as Lewis structures and VSEPR theory.

1. Colours of Transition Metal Complexes

- Why are most transition metal complexes brightly coloured but some aren’t?
- Why do the colours change as the ligand changes? As a typical example, consider three complexes of the nickel(II) ion:

\[
\begin{align*}
{[\text{Ni(H}_2\text{O)}_6]}^{2-} & \quad \text{green} \\
{[\text{Ni(NH}_3)_6]}^{2+} & \quad \text{deep blue} \\
{[\text{Ni(CN)}_4]}^{2-} & \quad \text{yellow}
\end{align*}
\]
Why do the colors change as the oxidation state of the metal changes, even for complexes of the same ligand? Here are some examples of this phenomenon:

\[
\begin{align*}
[\text{Cr(H}_2\text{O)}_6]^{2+} & \quad [\text{Cr(H}_2\text{O)}_6]^{3+} \\
\text{violet} & \quad \text{pale blue} \\
[\text{Co(NH}_3)_6]^{2+} & \quad [\text{Co(NH}_3)_6]^{3+} \\
\text{red} & \quad \text{yellow-brown} \\
[\text{NiF}_6]^{3-} & \quad [\text{NiF}_6]^{2-} \\
\text{violet} & \quad \text{red}
\end{align*}
\]

A variety of colors are observed for coordination complexes.

H\textsubscript{2}O and NH\textsubscript{4} are both colorless, but when they form a coordinate compound they change color!
The solutions of most octahedral Cu(II) complexes are blue. The visible spectrum for an aqueous solution of Cu(II), [Cu(H₂O₆)²⁺, shows that the absorption band spans the red-orange-yellow portion of the spectrum.

The color we see (blue) is the sum of the remaining colors that were not absorbed by the compound.

**UV-Vis absorption of Cu(II) complexes**

Crystal Field Theory - a partially set of d orbitals is usually required for a complex to be colored.

Transition metal complexes with d⁰ or d¹⁰ configurations are colorless, why?

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\begin{align*}
\text{ground state } & \text{Cu}^{2+} \\
\text{excited state } & \text{Cu}^{2+}
\end{align*}
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