23.3 Isomers of Coordination Complexes

Coordination Chemistry

Isomerism

- Isomers
- Structural Isomers
- Stereoisomers
- Geometrical Isomers
- Optical Isomers

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Geometry

Coordinate Number (CN):
Number of donor atoms bonded to metal

2 - Coordinate - linear
4 - Coordinate tetrahedral and square planar
   $ML_4$, Pt(II) is always CN = 4
6 - Octahedral
   $ML_6$, Cr(III) and Co(III) CN = 6

CN influence by
- size of metal ion.
- surrounding ligands.
  Small metal / large ligand - Low coordinate number
  Large metal / small ligand - High coordination number
  i.e., $FeF_6^{3-}$ and $FeCl_4^{-3}$

Example:
- $CuCl_2^-$, $Ag(NH_3)_2^+$, $AuCl_2^-$
- $Ni(CN)_4^{2-}$, $PdCl_2^{2-}$
- $Pt(NH_3)_4^{2+}$, $Cu(NH_3)_4^{2+}$
- $Cu(CN)_4^{3-}$, $Zn(NH_3)_4^{2+}$
- $CdCl_4^{2-}$, $MnCl_4^{2-}$
- $Cu(H_2O)_6^{3+}$, $V(CN)_6^{4+}$
- $Cu(NH_3)_4Cl_2^+$, $Co(en)_3^{3+}$
Historic Perspective

During early / mid 1800’s bonding was not well understood. Most widely accepted theory on bonding was the chain theory supported by Sophus Jorgensen (1837 - 1914). The structure of Co(NH₃)₆Cl₃ was explained in the classrooms using this theory in the late 1800’s. In 1890 Alfred Werner proposed a new bonding scheme and wrote a paper called “coordination theory”. In 1913 Werner won the 14th Noble Prize for his work.

<table>
<thead>
<tr>
<th>Traditional Formula</th>
<th>Werner’s Data*</th>
<th>Modern Formula</th>
<th>Charge of Complex Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Ions</td>
<td>Free Cl⁻</td>
<td></td>
</tr>
<tr>
<td>CoCl₃·6NH₃</td>
<td>4</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>CoCl₃·5NH₃</td>
<td>3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>CoCl₃·4NH₃</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>CoCl₃·3NH₃</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

*Moles per mole of compound.
Isomers -

**Same formula different properties.** i.e., $\text{N}_2\text{O} \rightarrow \text{NNO or NON}$

**Structural isomer**
- Compound with different atomic bond connectivity.
- Coordination sphere isomer
- Linkage isomer

**Stereoisomer**
- Same atomic connectivity but different arrangement.
- Geometrical isomer
- Optical isomer

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**ISOMERS**

Same chemical formula, but different properties

<table>
<thead>
<tr>
<th>Constitutional (structural) isomers</th>
<th>Stereoisomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atoms connected differently</td>
<td>Different spatial arrangement</td>
</tr>
<tr>
<td><strong>Coordination isomers</strong></td>
<td>Geometric (<em>cis</em>-trans) isomers (diastereomers)</td>
</tr>
<tr>
<td>Ligand and counter-ion exchange</td>
<td>Different arrangement around metal ion</td>
</tr>
<tr>
<td><strong>Linkage isomers</strong></td>
<td>Optical isomers (enantiomers)</td>
</tr>
<tr>
<td>Different donor atom</td>
<td>Nonsuperimposable mirror images</td>
</tr>
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</table>
Structural isomer-

Different Atomic connectivity: \( \text{Co(H}_2\text{O)}_6\text{Cl}_3 \)

Coordinate sphere isomer - Complexes in which the ligand is bonded differently to the metal.

\[
\begin{align*}
\text{Co} & \quad 3\text{Cl} \quad 6\text{H}_2\text{O} \\
\end{align*}
\]

1) six \( \text{H}_2\text{O} \) in coordination sphere.

\[
\begin{align*}
\text{Co(H}_2\text{O)}_6\text{Cl}_3 & \quad \text{Violet} \\
\end{align*}
\]

2) five \( \text{H}_2\text{O} \) and one \( \text{Cl} \) in coordination sphere.

\[
\begin{align*}
\text{Co(H}_2\text{O)}_5\text{Cl} & \quad \text{Cl} \cdot \text{H}_2\text{O} & \quad \text{Dark Green} \\
\end{align*}
\]

3) four \( \text{H}_2\text{O} \) and two \( \text{Cl} \) in coordination sphere.

\[
\begin{align*}
\text{Co(H}_2\text{O)}_4\text{Cl}_2 & \quad \text{Cl}_1 \cdot 2\text{H}_2\text{O} & \quad \text{Green} \\
\end{align*}
\]
Linkage Isomers

Linkage isomer - Isomer complexes in which the ligand coordinates to the metal by different donor atoms. i.e., Nitrite ion, NO$_2^-$

Nitro ligand as an N-donor

Nitrito ligand as an O-donor

Other ligand capable of switching donor atom
SCN$^-$, CN$^-$, 2.2’-bipyridine
Linkage Isomer of 2,2’-bipyridine

Two compounds formed by the linkage isomer of bpy is shown. Small changes in ligand bonding could result in dramatic chemical property change.
**Geometric Stereoisomer**

**Geometric isomer** - Compounds with similar atomic connectivity but different atomic arrangement in space.

**Diaminedichloroplatinum(II)**

Cisplatin

Diaminecis dichloroplatinum(II)

transplatin
diaminetrans dichloroplatinum(II)
Mirror Image

Mirror images cannot be exactly superimposed over each other. Complexes which form mirror images are called chiral.

Most of the human body is chiral (the hands). Enzymes are the most highly chiral substances known.
Optical Isomers

Optical isomer - Isomer complex in which the atomic connection are the same but arrangement is such that the two complexes are not superimposable.

Optical isomers are called enantiomer.

Chiral Complexes are also called enantiomers
Optical Inorganic Isomers

Enantiomer - Isomer that are mirror image to each other.
Handedness:

“R”

“S”

Molecules/Ions that have enantiomer are chiral
cis-trans-optical isomers

How many isomers are possible for [Co(en)_2Cl_2]^+ complex

Total of three, cis possesses enantiomeric pair and trans isomers.
Optical Isomer and Interaction with Light

Enantiomers rotate the plane of polarized light.

Dextrorotatory- “d” isomer
Complex which rotates plane of polarized light to the right.

Levorotatory- “l” isomer
Complex which rotates plane of polarized light to the left.

Chiral molecules are optically active because effect on light