B.Sc.(H) Chemistry
Semester - IV
Core Course - VIII (CC-VIII)
Inorganic Chemistry - III

I. Coordination Chemistry

14. Isomerism in Coordination Compounds

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Coordination Chemistry: 20 Lectures

Werner's theory, valence bond theory (inner and outer orbital complexes), electroneutrality principle and back bonding. Crystal field theory, measurement of 10 Dq (Δo), CFSE in weak and strong fields, pairing energies, factors affecting the magnitude of 10 Dq (Δo, Δt). Octahedral vs. tetrahedral coordination, tetragonal distortions from octahedral geometry Jahn-Teller theorem, square planar geometry. Qualitative aspect of Ligand field and MO Theory.

IUPAC nomenclature of coordination compounds, isomerism in coordination compounds. Stereochemistry of complexes with 4 and 6 coordination numbers. Chelate effect, polynuclear complexes, Labile and inert complexes.

Coverage:

1. Isomerism in Coordination Compounds

Isomerism

- **Our discussion of isomers will be largely limited to those with the same ligands arranged in different geometries. This is referred to as stereoisomers.**

Four-coordinate complexes:

Square-planar complexes may have *cis* and *trans* isomers. No chiral isomers (enantiomers) are possible when the molecule has a mirror plane.

***cis*- and *trans*-diamminedichloroplatinum(II)**

How about tetrahedral complexes? Chelate rings commonly impose a 'cis' structure. Why

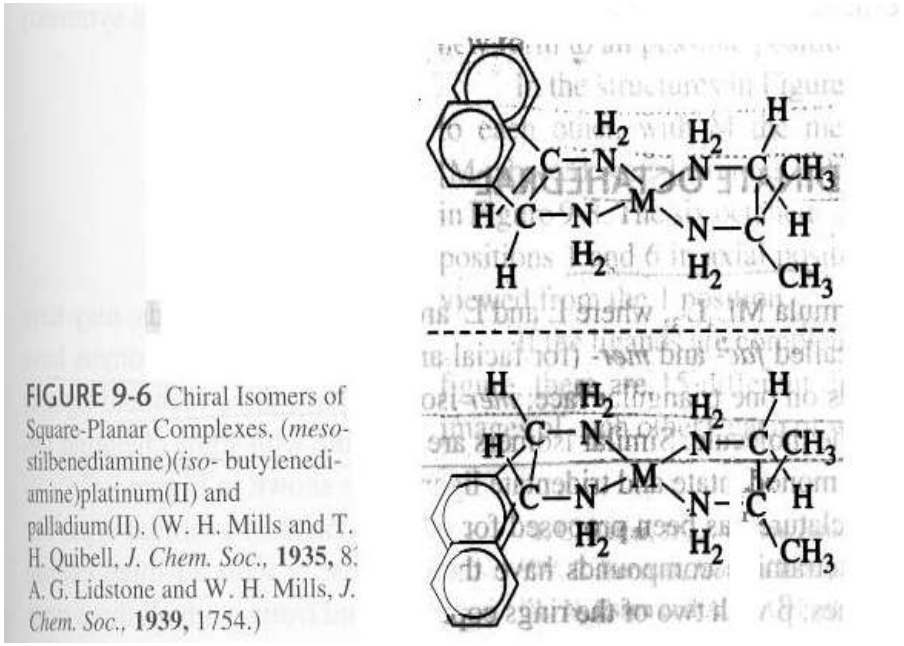


FIGURE 9-6 Chiral Isomers of Square-Planar Complexes. (*meso*-stilbenediamine)(*iso*- butylenediamine)platinum(II) and palladium(II). (W. H. Mills and T. H. Quibell, *J. Chem. Soc.*, **1935**, 8; A. G. Lidstone and W. H. Mills, *J. Chem. Soc.*, **1939**, 1754.)

Chirality

- **Mirror images are nonsuperimposable.**
- **A molecule can be chiral if it has no rotation-reflection axes (S_n)**
- **Chiral molecules have no symmetry elements or only have an axes of proper rotation (C_n).**

  CBrClFI, Tetrahedral molecule (different ligands)

  Octahedral molecules with bidentate or higher chelating ligands

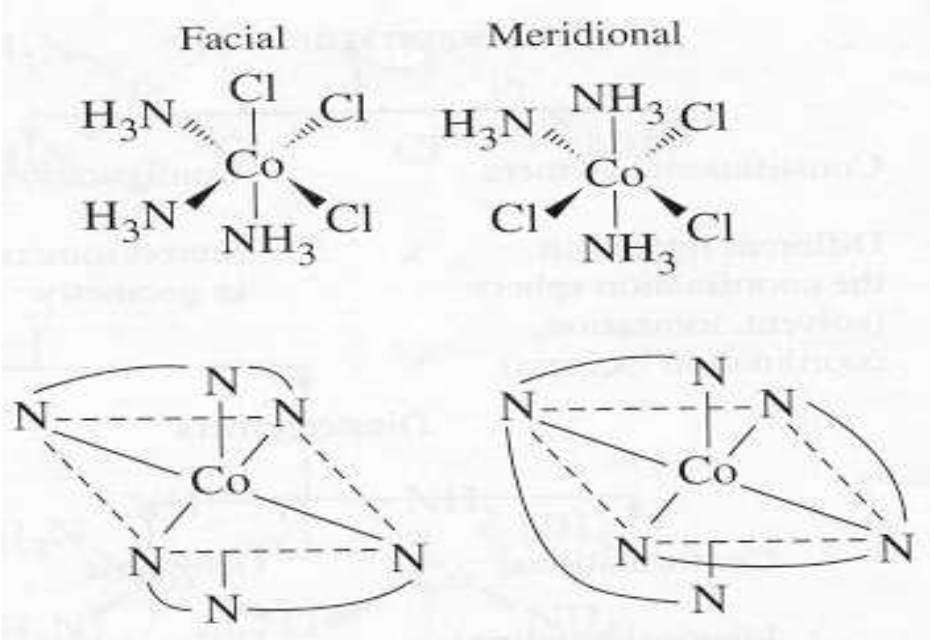
  Octahedral species with $[Ma_2b_2c_2]$, $[Mabc_2d_2]$, $[Mabcd_3]$, $[Mabcde_2]$, or [Mabcdef]

Six-Coordinate Octahedral Complexes

- **ML_3L_3**

  Fac isomers have three identical ligands on the same face.

  Mer isomers have three identical ligands in a plane bisecting the molecule.



Six-Coordinate Octahedral Complexes

- **The maximum number of isomers can be difficult to calculate (repeats).**
- **Placing a pair of ligands in the notation <ab> indicates that a and b are trans to each other.**

  [M<ab><cd><ef>], [Pt<pyNH_3><NO_2Cl><BrI>]
- **How many diastereoisomers in the above platinum compound (not mirror images)?**
- **Identify all isomers belonging to Ma_3bcd.**

Determining the Number of Isomers

Formula	*Number of stereoisomers*	*Pairs of enantiomers*
Ma_6	1	0
Ma_5b	1	0
Ma_4b_2	2	0
Ma_3b_3	2	0
Ma_4bc	2	0
Ma_3bcd	5	1
Ma_2bcde	15	6
Mabcdef	30	15
$Ma_2b_2c_2$	6	1
Ma_2b_2cd	8	2
Ma_3b_2c	3	0
M(AA)(BC)de	10	5
M(AB)(AB)cd	11	5
M(AB)(CD)ef	20	10
$M(AB)_3$	4	2
M(ABA)cde	9	3
$M(ABC)_2$	11	5
M(ABBA)cd	7	3
M(ABCBA)d	7	3

Capital letters represent chelating ligands, lowercase represent monodentate ligands.

Determining the Number of Isomers

- **Bailar method**
- **With restrictions (such as chelating agents) some isomers may be eliminated.**
- **Determine and identify the number if isomers.**

  $[Ma_2b_2cd]$ and [M(AA)bcde]

Combinations of Chelate Rings

- **Propellers and helices**

  Left- and right-handed propellers

- **Examine the movement of a propeller required to move it in a certain direction.**

  For a left-handed propeller, rotating it ccw would cause it to move away (Λ).

  For a right-handed propeller, rotating it cw would cause it to move away (Δ).

This is called 'handedness'. Many molecules possess it.

Tris(ethylenediamine)cobalt(III)

- **This molecule can be treated like a three-bladed propeller.**
- **Look down a three fold axis to determine the 'handedness' of this complex ion.**
  - **The direction of rotation required to pull the molecule away from you determines the handedness (Δ or Λ).**
- **Do this with you molecule set and rubber bands.**

Linkage (ambidentate) Isomerism

- **A few ligands may bond to the metal through different atoms.**

  SCN^- and NO_2^-

- **How would you expect hard acids to bond to the thiocyanate ligand?**
- **Solvents can also influence bonding.**

  High and low dielectric constants.
- **Steric effects of linkage isomerism**
- **Intramolecular conversion between linkages.**

  $[Co(NH_3)_5NO_2]^{+2}$.

Separation and Identification of Isomers

- **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.**

Separation and Identification of Chiral Isomers

- **Separations are performed with chiral counterions. The resulting physical properties will differ allowing separation.**
- **Rotation of polarized light will be opposite for two chiral isomers at a specific wavelength.**

  The direction of optical rotation can change with wavelength.

Circular Dichroism Meaurement

- **The difference in the absorption of right and left circularly polarized light is measured.**

$$\text{Circular dichroism} = \varepsilon_l - \varepsilon_r$$

Where ε_l and ε_r are the molar absorption coefficients for left and right circularly polarized light.

- **The light received by the detector is presented as the difference between the absorbances.**

Plane-Polarized Light Measurement

- **The plane of polarization is rotated when passing through a chiral substance.**

  Caused by a difference in the refractive indices of the right and left circularly polarized light.

$$\alpha = \frac{\eta_l - \eta_r}{\lambda}$$

  The optical rotation illustrates positive value on one side of the adsorption maximum and negative side on the other. This is termed as the Cotton effect.

THANK YOU