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CHEMISTRY
Paper 7 : Inorganic Chemistry-II (Metal-Ligand Bonding, Electronic Spectra and Magnetic Properties of Transition Metal Complexes)
Module 23 : Stereochemical Notation in Coordination Chemistry

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1. Learning Outcomes

After studying this module, you shall be able to

- Know about methods of the naming of chiral molecules
- Learn various methods to denote the absolute configuration of optical isomers
- Identify d-/l- System and R/S System for naming of complexes
- Identify Λ/Δ notation and δ/λ System for naming of complexes
- Allocate stereochemical notation to the given optically active complex

2. Stereochemical Notation in Coordination Chemistry: Absolute Configuration of Complexes

Several different ways to represent an octahedral metal ion are shown in figure1;

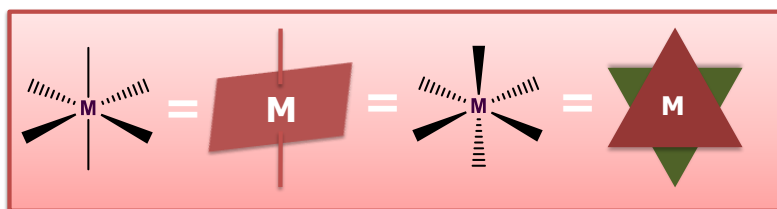


Figure 1

Which way we chose depends on the method for naming the chiral complex. Although the naming of chiral molecules is a tedious job, but various methods have been proposed to denote the absolute configuration of optical isomers.

1. *d*- and *l*- System
2. R and S System
3. Lambda Λ and Delta Δ notation
4. Delta δ and Lambda λ System

Let us briefly discuss means of denoting such configurations.

3. *d*- and *l*- System

The simplest method is the notation on the basis of the direction of rotation of plane polarized light. Dextrorotatory means, the isomer rotates plane polarized light to right side and it is labeled as the dextro, or (+), or *d*, isomer (Latin *dexter*, "right"). On the other hand, mirror image of the isomer rotates plane polarized light to left and known as **levorotatory** and is labeled as the leavo, or (-), or *l*, isomer (Latin *laevus*, "left").

Normally in the case of coordination complexes, $(+)_{\lambda}$ and $(-)_{\lambda}$ are used to designate the sign of rotation of plane polarized light at the specified wavelength, λ . When the sign appears without the wavelength noted, the wavelength is assumed to be that of a sodium D line (589 and 589.6 nm). For example, $(+)_{589}\text{-}[\text{Co}(\text{en})_3]^{3+}$, which is dextrorotatory with respect to light of sodium D line.

This method of naming the complexes is not found to be appropriate because, when optical activity of the tris(1,2-diaminoethane) M(III) complexes (M= Rh(III) and Co(III)) was measured at sodium D line (589nm), they rotate the plane polarized light in opposite directions; however, they are having the identical absolute configuration (Figure 2).

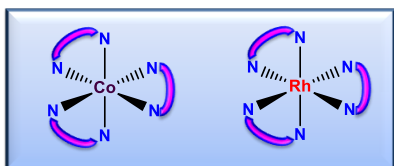


Figure 2

4. R and S System

R and S are used to describe the absolute configurations of dissymmetric complexes according to Cahn-Ingold-Prelog (CIP) system. This method is commonly used in organic chemistry. The IUPAC rules suggest that for general octahedral complexes C/A scheme is convenient to use. C/A scheme works only for the complexes having monodentate ligands. In coordination chemistry CIP rule by Cahn, Ingold and Prelog is famous to determine the priority for coordination complexes i.e. based on mononuclear coordination systems. The ligands are arranged on the basis of atomic number such as highest atomic number have highest priority and have smallest CIP number.

For example, hypothetical complex $[\text{Fe}(\text{III}) \text{Cl} \text{ Br} \text{ I} (\text{NH}_3) (\text{NO}_2) (\text{SCN})]^{2-}$ would assign the priorities to the groups I as 1, Br^- as 2, Cl^- as 3, SCN^- as 4, NO_2^- as 5 and NH_3 as 6. In one such isomer ligand I and Cl^- , and Br^- and NO_2^- were found to be *trans*- to each other (Figure 3)

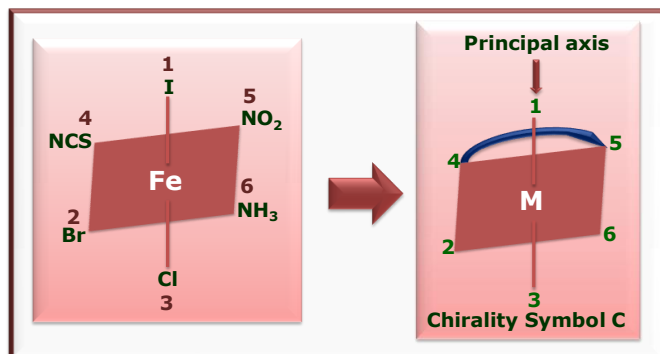


Figure 3

The reference axis for an octahedral centre is that axis containing the group of CIP priority 1 and the *trans* ligating atom of lowest possible priority (highest numerical value). The atoms in the coordination plane perpendicular to the reference axis are viewed from the ligand having that highest priority (CIP priority 1) and the clockwise and anticlockwise sequences of priority numbers are compared. The structure is assigned the symbol C or A, according to whether the clockwise (C) or anticlockwise (A) sequence is lower at the first point of difference.

The reference axis for the complex shown in figure 3, will be axis containing I⁻ and Cl⁻ ligands. According to rules rotation is clockwise, thus the structure is assigned the symbol C.

Another isomer of the same complex $[\text{Fe}(\text{III}) \text{Cl} \text{Br} \text{I} (\text{NH}_3) (\text{NO}_2) (\text{SCN})]^{2-}$ is shown in figure 4. For this isomer the ligand I⁻ and Br⁻, and Cl⁻ and NO₂⁻ were found to be *trans*- to each other. The reference axis for this complex will be axis containing I⁻ and Br⁻ ligands. According to rules rotation is anticlockwise, thus the structure is assigned the symbol A.

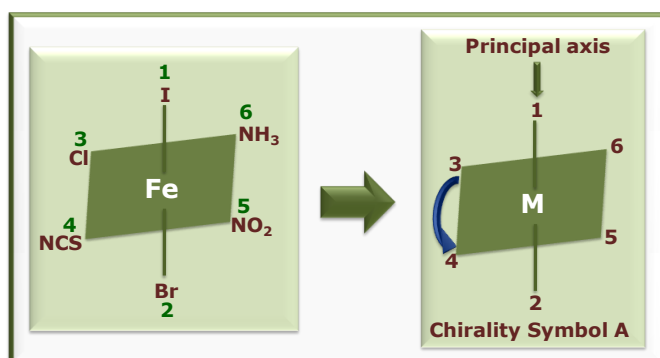


Figure 4

The two optical isomers of $[\text{Co}(\text{en})_3]^{3+}$ have identical chemical properties

Just denoting their absolute configuration does not give any information regarding the direction in which they rotate plane-polarized light

This can be determined from measurement and then the isomers are further distinguished by using the prefixes (-) and (+)

Depending whether they rotate the polarized light left or right.

For tetrahedral complexes, R and S would be used in a similar method to tetrahedral carbon species and although it is predicted that tetrahedral complexes with 4 different ligands should be able to give rise to optical isomers, in general they are too labile and cannot be isolated.

5. Lambda Λ and Delta Δ notation

For dissymmetric complexes of bis- and tris-bidentate ligands, the absolute configuration can be described using Lambda Λ and Delta Δ notations. Delta Δ is used when chelate rings describe right-handed helix, however, Lambda Λ is used when they describe left-handed helix.

The handedness can be understood by taking the example of propellers (Figure 5). These propellers are enantiomers of each other and they can describe a left-handed (A) and a right-handed (B) helix on rotating and moving through space. If we fix our eye on one blade, that point will describe a helix as the propeller rotates while moving through the space. The two propellers in figure 5 are different in their direction of rotation. Propellor (A) describes a left-handed helix, however, propellor (B) a right-handed helix on moving through the space.

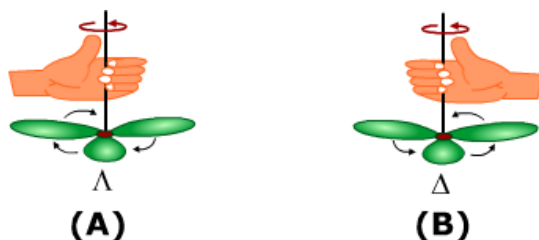
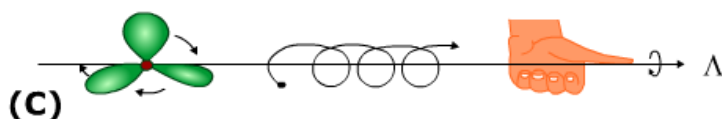
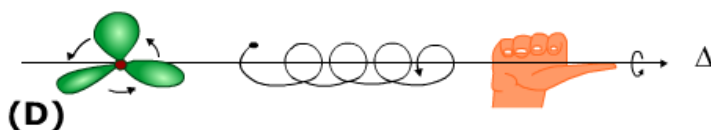


Illustration of the left- (Λ) and right handedness (Δ) of enantiomeric three bladed propellers.



A left-handed propellor traces out a left-handed helix on traveling through space.



A right-handed propellor traces out a right-handed helix on traveling through space.

Figure 5

A tris(bidentate ligand) metal complex can trace out a left-handed or a right-handed helix on rotating and moving through space, exactly in a same way a propellor have helices.

Procedure for determining handedness

1. Rotate the figure to place one ring horizontally across the back, at the top of one of the triangular faces.
2. Imagine the ring in the front triangular face as having originally been parallel to the ring at the back. Determine what rotation is required to obtain the actual configuration.
3. If the rotation from step 2 is counterclockwise, the structure is designed Lambda Λ . If the rotation is clockwise, the designation is Delta Δ . (Figure6)

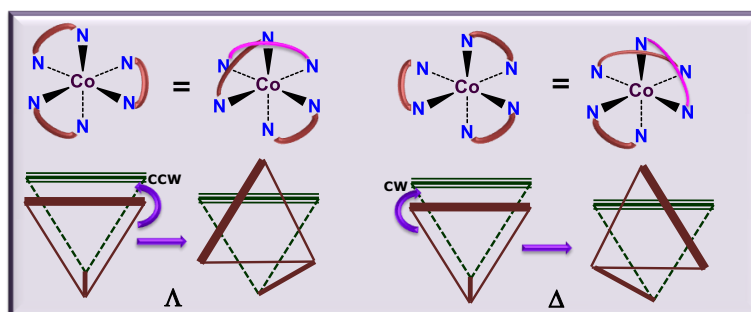


Figure 6

Figure 7 illustrates another way of determining handedness is to look directly at a triangular face of the octahedron. The three nitrogen atoms shown on the upper triangular face of the octahedron are chosen to represent one of the binding sites in each of the three ligands, however, each of the nitrogen atoms on the opposite or the lower triangular face are connected to one of those on the upper face with an arc representing the ligand backbone. The right-handed or Δ isomer requires the movement of backbone from the upper triangle to the lower one in clockwise direction. On the other hand, in order to change the configuration of upper triangle to lower one. It undergoes counterclockwise orientation and the prefix for this isomer is Λ . For example two optical isomers of $[\text{Co}(\text{en})_3]^{3+}$ are shown in figure 7. In the left isomer, the movement of backbone from the upper triangle to the lower one is in counterclockwise direction, so this isomer is left-handed isomer and the prefix for this isomer is Λ . However, for the isomer on the right side of the figure, the movement of backbone from the upper triangle to the lower one is in clockwise direction, so this isomer is right-handed isomer and the prefix for this isomer is Δ .

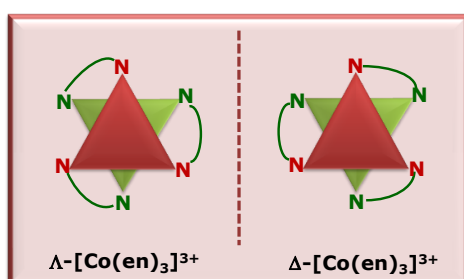


Figure 7

Another example, $[\text{Co}(\text{ox})_3]^{3-}$ is shown in figure 8. In the left isomer, the movement of backbone from the upper triangle to the lower one is in clockwise direction, so this isomer is right-handed isomer and the prefix for this isomer is Δ . However, for the isomer on the right side of the figure, the movement of backbone from the upper triangle to the lower one is in counterclockwise direction, so this isomer is left-handed isomer and the prefix for this isomer is Λ .

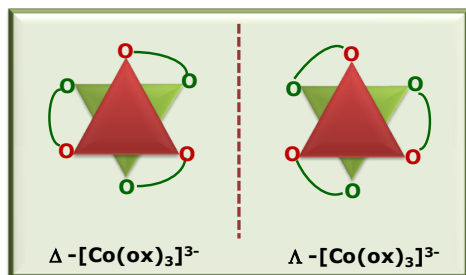


Figure 8

6. Lambda λ and Delta δ System

Notation, δ and λ are used to describe the conformations of individual chelate rings. Delta δ denotes a ring of right-handed helicity and Lambda λ denotes a ring of left-handed helicity. When a bidentate ligand is bonded to a metal ion, a 5- or 6-membered chelate ring is formed (figure 9). The number depends on the number of atoms in the ligand "backbone". Although the two donor atoms and the metal must be in the same plane, backbone atoms are not co-planar with them, and two conformations are possible for the ligand. This is shown below for the ligand ethylenediamine. (Assume that the metal is behind the ligand, away from the viewer.)

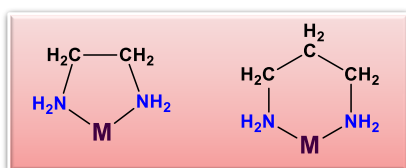


Figure 9

δ and λ system is available to designate the "twisting" of the backbone atoms in chelate rings (relative to the N-M-N plane of atoms). Consider the ligand bonded to metal as shown above. If all five atoms involved are imagined to be in a single plane this is called a "gauche" conformation. Although not met in practice, "gauche" is the starting point for analyzing actual conformations. Relative to all atoms in the same plane, note how the backbone would need to rotate in order to adopt each conformation shown in figure 10. On the left, backbone atoms would be rotated in a clockwise manner. On the right, backbone atoms would be rotated in a counter-clockwise manner. The symbols used are lower-case Greek letters *delta* (δ) and *lambda* (λ) respectively.

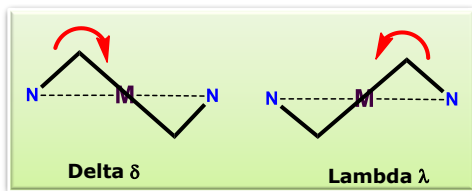


Figure 10

The conformation of one ligand is independent of the others. For a tris(bidentate) complex having the absolute configuration delta Δ and three ligand chains with conformations λ , λ and δ , the designation for the complex is written as Δ - $\lambda\lambda\delta$. This informs that, and two of the rings have lambda conformations while the third has delta conformation. For example, $[\text{Co}(\text{en})_3]^{3+}$ complex is shown in figure 11. Absolute configuration of the complex is Δ , compare the figure at right. The conformations of three bidentate ligands are δ , λ , λ , as labeled in figure 11 and shown below in different perspective (Figure 12).

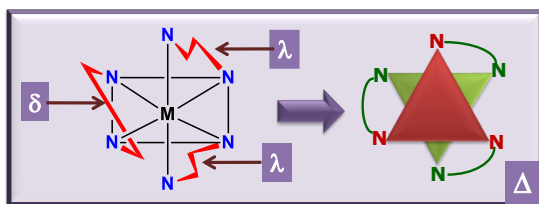


Figure 11

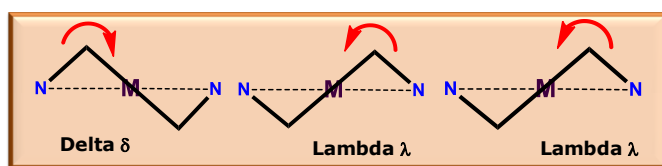
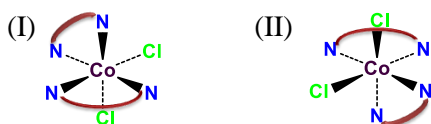


Figure 12

7. Study Questions

Question1: Assign the Lambda Λ or Delta Δ , chirality label for the complexes, cis-dichlorobis(ethylenediamine)cobalt(III), shown below:



Solution:

(I) Rotate the figure 180° about the vertical axis in such a way that one ring comes across the back and other connecting the top and the front right positions (Figure 13). If this front ring was originally parallel to the back one, a clockwise rotation would put it into the correct position. Therefore, the structure is Delta Δ . Thus the name of this complex would be Δ -cis-dichlorobis(ethylenediamine)cobalt(III).

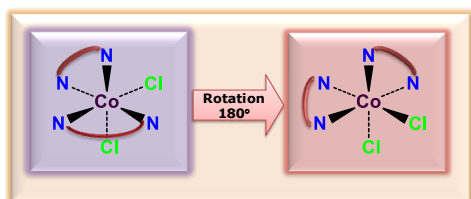


Figure 13

Alternate method: Rotate the figure 180° about the vertical axis in such a way that one ring comes across the back and other connecting the top and the front right positions. Now draw the upper and lower a triangular face of the octahedron (Figure 14). The two nitrogen atoms shown on the upper triangular face of the octahedron are chosen to represent one of the binding sites in each of the two ligands, however, each of the nitrogen atoms on the opposite or the lower triangular face are connected to one of those on the upper face with an arc representing the ligand backbone. The movement of backbone from the upper triangle to the lower one is in clockwise direction means right-handed or Δ isomer. Thus the name of this complex would be Δ -cis-dichlorobis(ethylenediamine)cobalt(III).

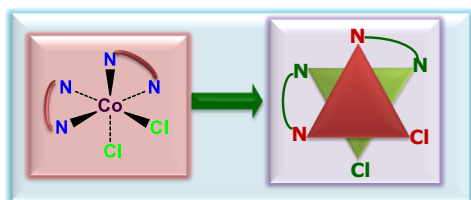


Figure 14

(II) Rotate the figure 90° about the vertical axis in such a way that one ring comes across the back and other connecting the top and the front right positions (Figure 15). If this front ring was originally parallel to the back one, a counterclockwise rotation would put it into the correct position. Therefore, the structure is Lambda Λ . Thus the name of this complex would be Λ -cis-dichlorobis(ethylenediamine)cobalt(III).

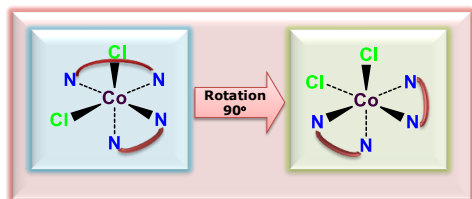


Figure 15

Alternate method: Rotate the figure 90° about the vertical axis in such a way that one ring comes across the back and other connecting the top and the front right positions (Figure 16). Now draw the upper and lower a triangular face of the octahedron. The two nitrogen atoms shown on the upper triangular face of the octahedron are chosen to represent one of the binding sites in each of the two ligands, however, each of the nitrogen atoms on the opposite or the lower triangular face are connected to one of those on the upper face with an arc representing the ligand backbone. The movement of backbone from the upper triangle to the lower one is in counterclockwise direction means left-handed or Λ isomer. Thus the name of this complex would be Λ -cis-dichlorobis(ethylenediamine)cobalt(III).

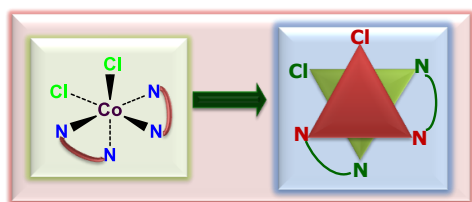
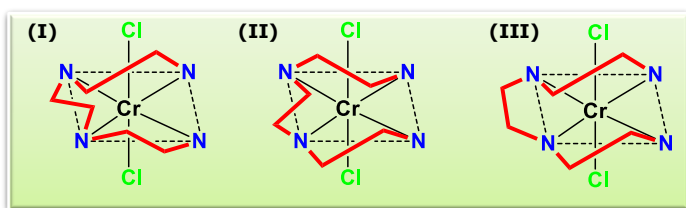
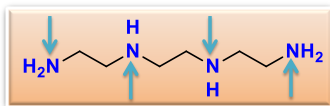


Figure 16

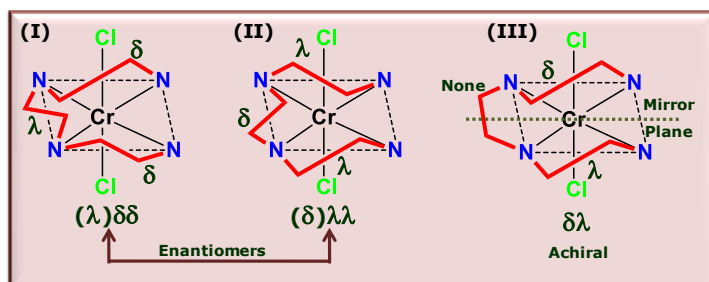
Question 2: Assign chirality label δ and λ for the conformations of chelate rings for the chiral structures of the complex, *trans*-dichloro(trien)chromium(III), *trans*-[Cr(trien)Cl₂]⁺ shown below: (Where trien refers to triethylenetetramine which is tetradentate ligand and form three chelate ring around the metal center)



Solution: The structure of the triethylenetetramine is shown in figure and also the four binding sites of the ligand are shown with the help of blue arrows.



The conformations of three ethylene rings are established by using same method discussed under section.



8. Summary

In this module, we discussed

- Various methods to denote the absolute configuration of enantiomers
- Four following methods for the naming of complexes:
 - 1) d-/l- System
 - 2) R/S System
 - 3) Λ/Δ notation
 - 4) δ/λ System