❖ Racemization of Tris Chelate Complexes

The tris chelate metal complexes exist in two enantiomeric forms, called as Λ and Δ configurations.

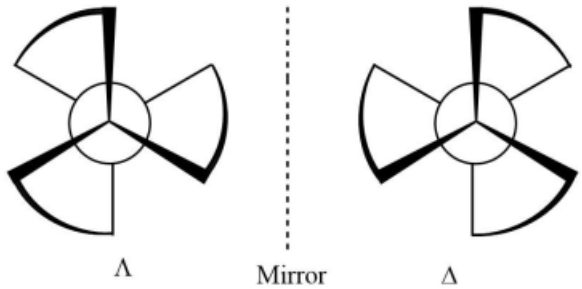


Figure 18. Enantiomeric forms of octahedral tris chelate complexes.

The point group symmetry for the above system D_3. There are also geometrical isomers when the bidentate ligands are unsymmetrical in nature like glycinato. The total number isomer, in that case, is four as:

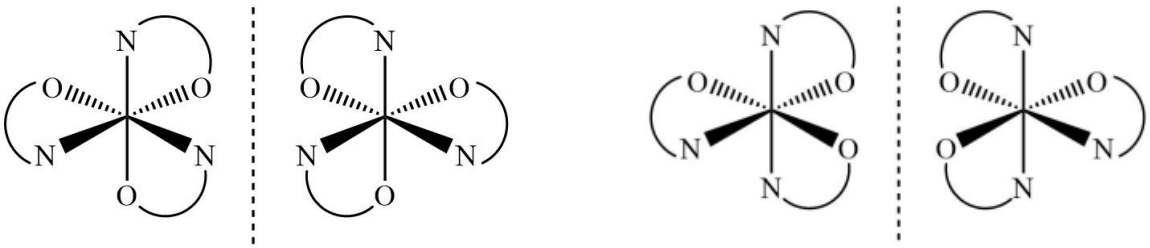
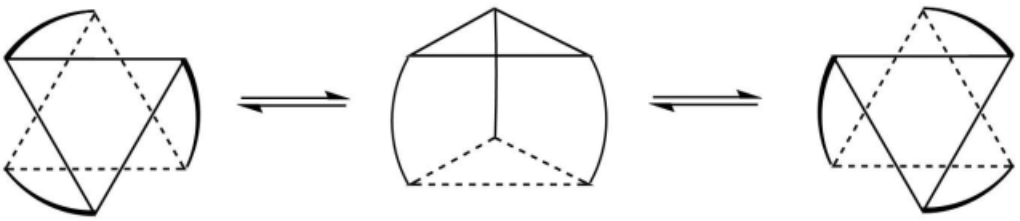


Figure 19. Enantiomeric forms of octahedral tris chelate complexes with the unsymmetrical ligand.

The interconversion or the racemization of tris chelate complexes in case symmetrical ligands can take place via with or without the rupturing of the metal-ligand bond.

1. Racemization without the breakage of metal-ligand bond: The two most common processes suggested for the interconversion of the two enantiomeric forms are the trigonal or Bailer twist and the rhombic or Ray-Dutt twist. Both of the processes can be visualized from the following mechanism.



(a)

(b)

Figure 20. Racemization of tris chelate complexes through (a) trigonal or Bailer twist (b) rhombic or Ray-Dutt twist.

The Bailar twist mechanism proposes that the racemization of octahedral metal complexes with three bidentate rings normally occurs via the formation of an intermediate of trigonal prismatic symmetry (D_{3h} point group). In honor of John C. Bailar, Jr., the inventor of the process, the pathway is called as Bailar twist. The second route is called the Ray-Dutt twist, a mechanism proposed also for the racemization of octahedral metal complexes with three bidentate chelate rings. These complexes usually adopt an octahedral geometry in their ground states and are therefore optically active. The Rây-Dutt pathway includes the formation of an intermediate species with C_{2v} point group symmetry. The name Rây-Dutt twist is in the honor of P. C. Rây and N. K. Dutt, the inorganic chemists who suggested this mechanism.

2. Racemization with the breakage of metal-ligand bond: There are four different possible pathways suggested for the interconversion of the two enantiomeric forms of tris chelate complexes through the dissociative mechanism. After the detachment of one of the atoms of the bidentate ligand, a five-coordinated intermediate with trigonal-bipyramidal or square-pyramidal geometry is formed which converts into another enantiomer afterward. The whole process can be visualized as follows However, it is also observed that the square-pyramidal intermediate may have a weakly bonded solvent molecule at the sixth site in some cases.

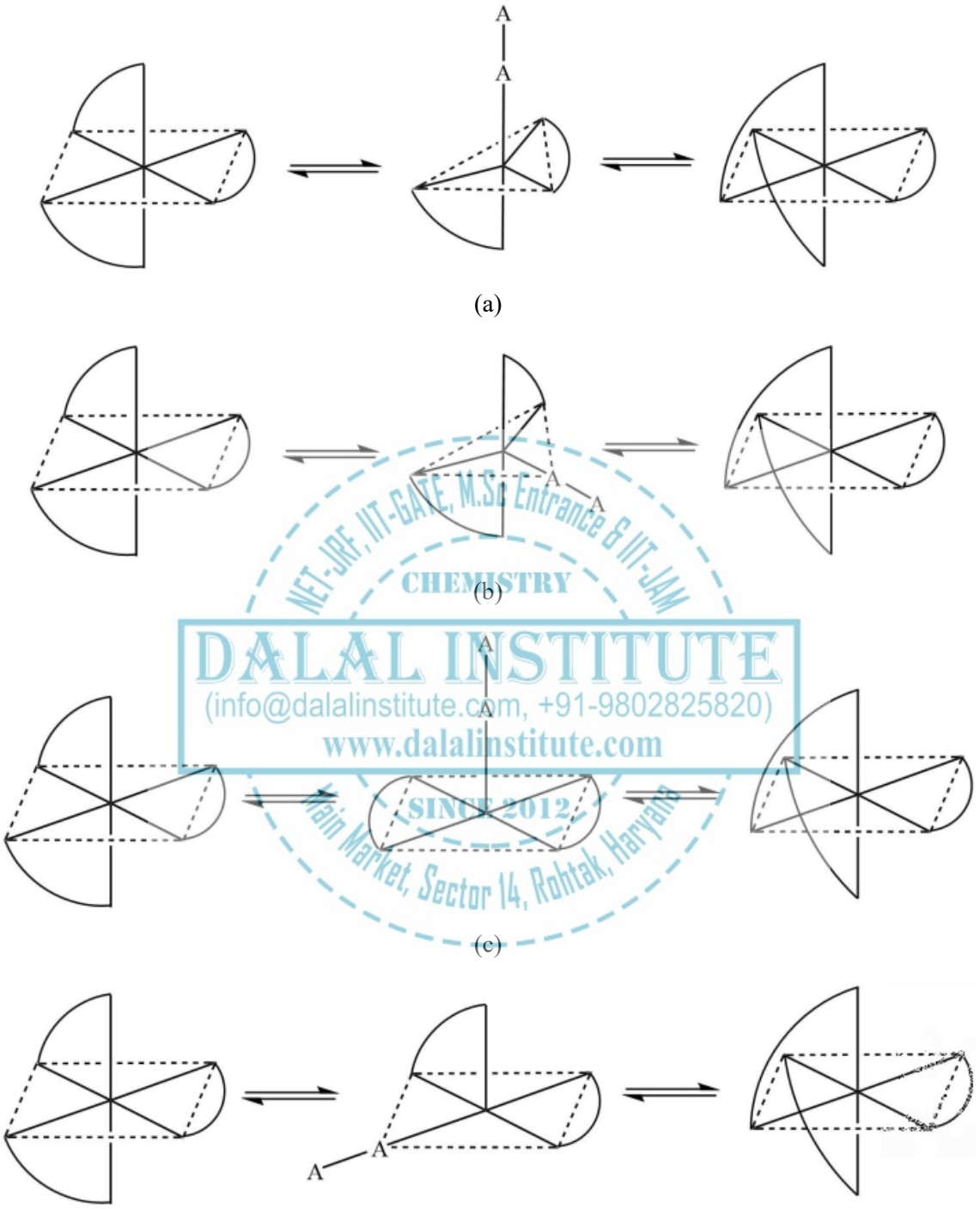


Figure 21. Racemization of tris chelate complexes through ring-opening mechanism via (a,b) trigonal-bipyramidal and (c,d) square-pyramidal intermediate.

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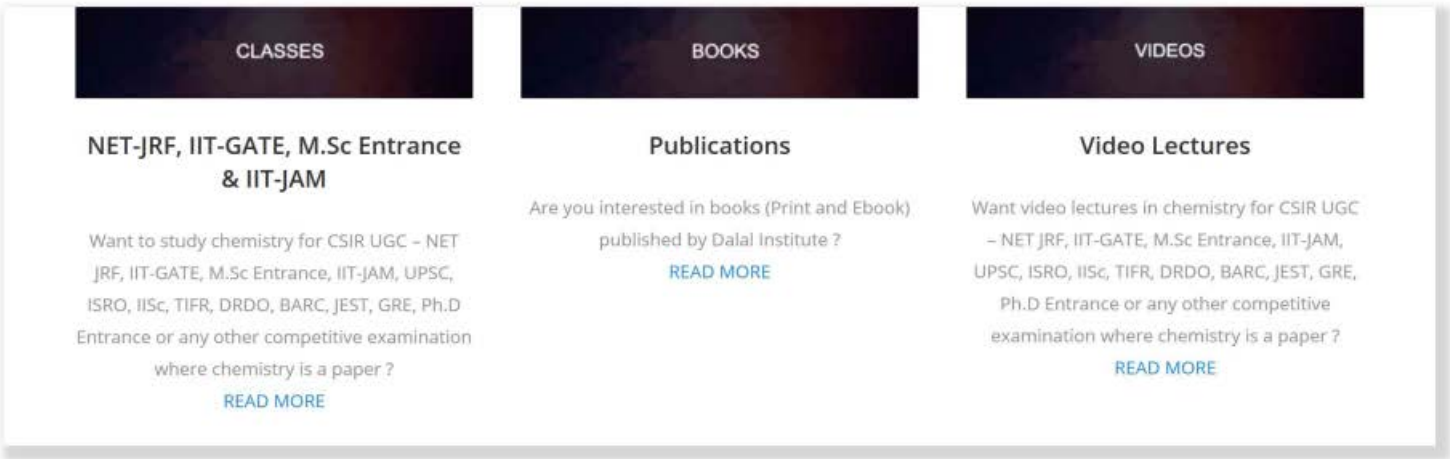

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