

### ❖ Racemization of Tris Chelate Complexes

The tris chelate metal complexes exist in two enantiomeric forms, called as  $\Lambda$  and  $\Delta$  configurations.

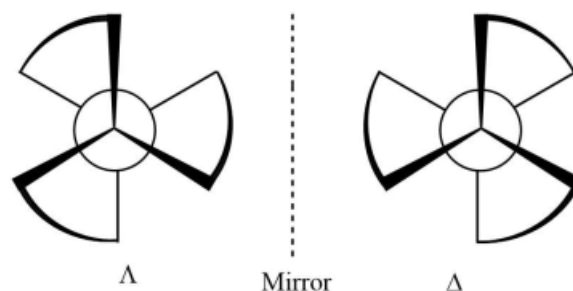


Figure 18. Enantiomeric forms of octahedral tris chelate complexes.

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

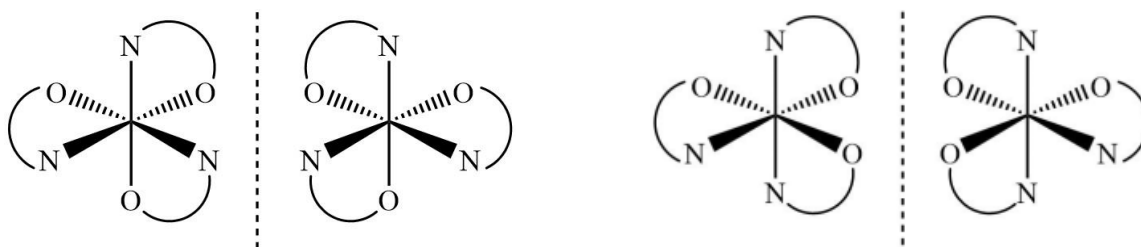


Figure 19. Enantiomeric forms of octahedral tris chelate complexes with the unsymmetrical ligand.

#### LEGAL NOTICE

This document is an excerpt from the book entitled “A Textbook of Inorganic Chemistry – Volume 1 by Mandeep Dalal”, and is the intellectual property of the Author/Publisher. The content of this document is protected by international copyright law and is valid only for the personal preview of the user who has originally downloaded it from the publisher’s website ([www.dalalinstitute.com](http://www.dalalinstitute.com)). Any act of copying (including plagiarizing its language) or sharing this document will result in severe civil and criminal prosecution to the maximum extent possible under law.

The interconversion or the racemization of tris chelate complexes in case of 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 Bailar twist and the rhombic or Ray-Dutt twist. Both of the processes can be visualized from the following mechanism.

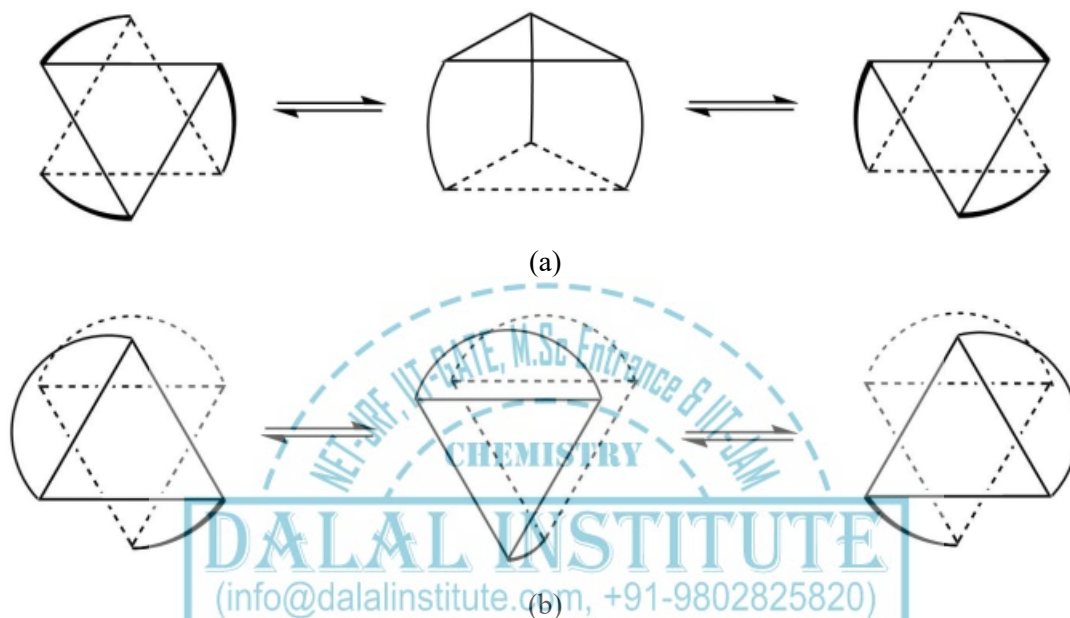


Figure 20. Racemization of tris chelate complexes through (a) trigonal or Bailar twist (b) rhombic or Ray-Dutt twist.

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 Ray-Dutt pathway includes the formation of an intermediate species with  $C_{2v}$  point group symmetry. The name Ray-Dutt twist is in the honor of P. C. Ray 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.

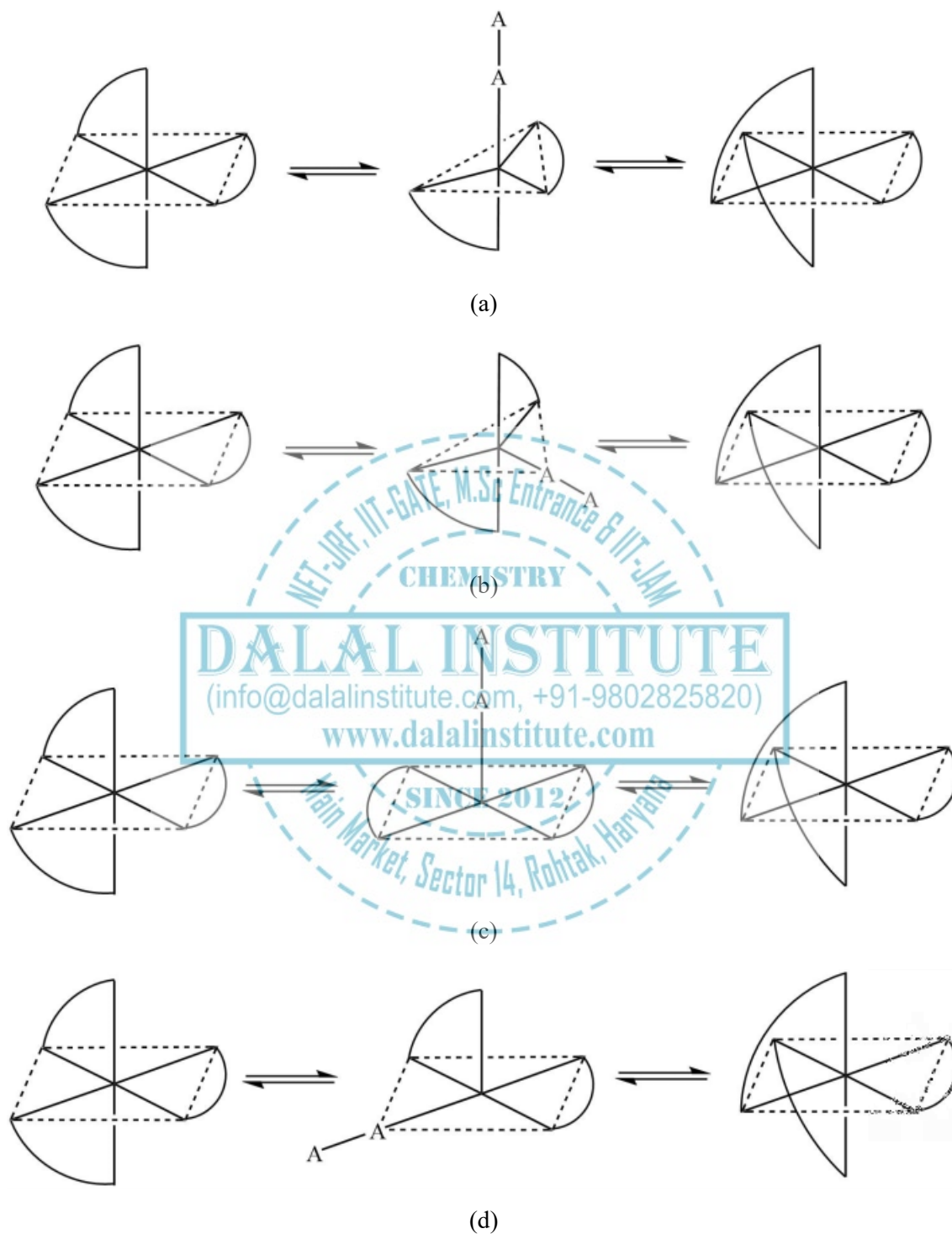


Figure 21. Racemization of tris chelate complexes through ring-opening mechanism via (a,b) trigonal-bipyramidal and (c,d) square-pyramidal intermediate.

## LEGAL NOTICE

This document is an excerpt from the book entitled “A Textbook of Inorganic Chemistry – Volume 1 by Mandeep Dalal”, and is the intellectual property of the Author/Publisher. The content of this document is protected by international copyright law and is valid only for the personal preview of the user who has originally downloaded it from the publisher’s website ([www.dalalinstitute.com](http://www.dalalinstitute.com)). Any act of copying (including plagiarizing its language) or sharing this document will result in severe civil and criminal prosecution to the maximum extent possible under law.



*This is a low resolution version only for preview purpose. If you want to read the full book, please consider buying.*

**Buy the complete book with TOC navigation, high resolution images and no watermark.**

## Home

### CLASSES

#### NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM

Want to study chemistry for CSIR UGC - NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

[READ MORE](#)

### BOOKS

#### Publications

Are you interested in books (Print and Ebook) published by Dalal Institute ?

[READ MORE](#)

### VIDEOS

#### Video Lectures

Want video lectures in chemistry for CSIR UGC - NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

[READ MORE](#)

**Home:** <https://www.dalalinstitute.com/>

**Classes:** <https://www.dalalinstitute.com/classes/>

**Books:** <https://www.dalalinstitute.com/books/>

**Videos:** <https://www.dalalinstitute.com/videos/>

**Location:** <https://www.dalalinstitute.com/location/>

**Contact Us:** <https://www.dalalinstitute.com/contact-us/>

**About Us:** <https://www.dalalinstitute.com/about-us/>

#### Postgraduate Level Classes (NET-JRF & IIT-GATE)

##### Admission

[Regular Program](#)  
[Test Series](#)

[Distance Learning](#)  
[Result](#)

#### Undergraduate Level Classes (M.Sc Entrance & IIT-JAM)

##### Admission

[Regular Program](#)  
[Test Series](#)

[Distance Learning](#)  
[Result](#)

#### A Textbook of Inorganic Chemistry – Volume 1

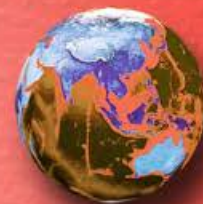
“A Textbook of Inorganic Chemistry – Volume 1 by Mandeep Dalal” is now available globally; including India, America and most of the European continent. Please ask at your local bookshop or get it online here.

[READ MORE](#)

*Join the revolution by becoming a part of our community and get all of the member benefits like downloading any PDF document for your personal preview.*

[Sign Up](#)

International  
Edition



# A TEXTBOOK OF INORGANIC CHEMISTRY

**Volume I**

**MANDEEP DALAL**



*First Edition*

**DALAL INSTITUTE**

# Table of Contents

<b>CHAPTER 1</b> .....	<b>11</b>
<b>Stereochemistry and Bonding in Main Group Compounds:</b> .....	<b>11</b>
❖ VSEPR Theory .....	11
❖ $d\pi-p\pi$ Bonds .....	23
❖ Bent Rule and Energetic of Hybridization.....	28
❖ Problems .....	42
❖ Bibliography .....	43
<b>CHAPTER 2</b> .....	<b>44</b>
<b>Metal-Ligand Equilibria in Solution:</b> .....	<b>44</b>
❖ Stepwise and Overall Formation Constants and Their Interactions .....	44
❖ Trends in Stepwise Constants.....	46
❖ Factors Affecting Stability of Metal Complexes with Reference to the Nature of Metal Ion and Ligand.....	49
❖ Chelate Effect and Its Thermodynamic Origin.....	56
❖ Determination of Binary Formation Constants by pH-metry and Spectrophotometry.....	63
❖ Problems .....	68
❖ Bibliography .....	69
<b>CHAPTER 3</b> .....	<b>70</b>
<b>Reaction Mechanism of Transition Metal Complexes – I:</b> .....	<b>70</b>
❖ Inert and Labile Complexes.....	70
❖ Mechanisms for Ligand Replacement Reactions .....	77
❖ Formation of Complexes from Aquo Ions.....	82
❖ Ligand Displacement Reactions in Octahedral Complexes- Acid Hydrolysis, Base Hydrolysis....	86
❖ Racemization of Tris Chelate Complexes .....	89
❖ Electrophilic Attack on Ligands .....	92
❖ Problems .....	94
❖ Bibliography .....	95

<b>CHAPTER 4</b> .....	<b>96</b>
<b>Reaction Mechanism of Transition Metal Complexes – II:</b> .....	96
❖ Mechanism of Ligand Displacement Reactions in Square Planar Complexes.....	96
❖ The Trans Effect.....	98
❖ Theories of Trans Effect.....	103
❖ Mechanism of Electron Transfer Reactions – Types; Outer Sphere Electron Transfer Mechanism and Inner Sphere Electron Transfer Mechanism.....	106
❖ Electron Exchange.....	117
❖ Problems.....	121
❖ Bibliography.....	122
<b>CHAPTER 5</b> .....	<b>123</b>
<b>Isopoly and Heteropoly Acids and Salts:</b> .....	123
❖ Isopoly and Heteropoly Acids and Salts of Mo and W: Structures of Isopoly and Heteropoly Anions .....	123
❖ Problems.....	152
❖ Bibliography.....	153
<b>CHAPTER 6</b> .....	<b>154</b>
<b>Crystal Structures:</b> .....	154
❖ Structures of Some Binary and Ternary Compounds Such as Fluorite, Antifluorite, Rutile, Antirutile, Cristobalite, Layer Lattices - $\text{CdI}_2$ , $\text{BiI}_3$ ; $\text{ReO}_3$ , $\text{Mn}_2\text{O}_3$ , Corundum, Pervoskite, Ilmenite and Calcite.....	154
❖ Problems.....	178
❖ Bibliography.....	179
<b>CHAPTER 7</b> .....	<b>180</b>
<b>Metal-Ligand Bonding:</b> .....	180
❖ Limitation of Crystal Field Theory.....	180
❖ Molecular Orbital Theory – Octahedral, Tetrahedral or Square Planar Complexes.....	184
❖ $\pi$ -Bonding and Molecular Orbital Theory .....	198
❖ Problems.....	212
❖ Bibliography.....	213



<b>CHAPTER 8 .....</b>	<b>214</b>
<b>Electronic Spectra of Transition Metal Complexes: .....</b>	<b>214</b>
❖ Spectroscopic Ground States .....	214
❖ Correlation and Spin-Orbit Coupling in Free Ions for 1st Series of Transition Metals.....	243
❖ Orgel and Tanabe-Sugano Diagrams for Transition Metal Complexes ( $d^1 - d^9$ States).....	248
❖ Calculation of $Dq$ , $B$ and $\beta$ Parameters .....	280
❖ Effect of Distortion on the $d$ -Orbital Energy Levels .....	300
❖ Structural Evidence from Electronic Spectrum .....	307
❖ Jahn-Teller Effect .....	312
❖ Spectrochemical and Nephelauxetic Series .....	324
❖ Charge Transfer Spectra .....	328
❖ Electronic Spectra of Molecular Addition Compounds.....	336
❖ Problems .....	340
❖ Bibliography .....	341
<b>CHAPTER 9 .....</b>	<b>342</b>
<b>Magnetic Properties of Transition Metal Complexes: .....</b>	<b>342</b>
❖ Elementary Theory of Magneto-Chemistry .....	342
❖ Guoy's Method for Determination of Magnetic Susceptibility .....	351
❖ Calculation of Magnetic Moments .....	354
❖ Magnetic Properties of Free Ions.....	359
❖ Orbital Contribution: Effect of Ligand-Field .....	362
❖ Application of Magneto-Chemistry in Structure Determination .....	370
❖ Magnetic Exchange Coupling and Spin State Cross Over .....	375
❖ Problems .....	384
❖ Bibliography .....	385
<b>CHAPTER 10 .....</b>	<b>386</b>
<b>Metal Clusters: .....</b>	<b>386</b>
❖ Structure and Bonding in Higher Boranes.....	386
❖ Wade's Rules.....	401

❖ Carboranes.....	407
❖ Metal Carbonyl Clusters- Low Nuclearity Carbonyl Clusters.....	412
❖ Total Electron Count (TEC).....	417
❖ Problems.....	424
❖ Bibliography.....	425
<b>CHAPTER 11.....</b>	<b>426</b>
<b>Metal-II Complexes: .....</b>	<b>426</b>
❖ Metal Carbonyls: Structure and Bonding.....	426
❖ Vibrational Spectra of Metal Carbonyls for Bonding and Structure Elucidation.....	439
❖ Important Reactions of Metal Carbonyls.....	446
❖ Preparation, Bonding, Structure and Important Reactions of Transition Metal Nitrosyl, Dinitrogen and Dioxygen Complexes.....	450
❖ Tertiary Phosphine as Ligand.....	463
❖ Problems.....	469
❖ Bibliography.....	470
<b>INDEX.....</b>	<b>471</b>



*Mandeep Dalal*

*(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)*

*Founder & Director, Dalal Institute*

*Contact No: +91-9802825820*

*Homepage: [www.mandeepdalal.com](http://www.mandeepdalal.com)*

*E-Mail: [dr.mandeep.dalal@gmail.com](mailto:dr.mandeep.dalal@gmail.com)*

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands) .

*Other Books by the Author*

**A TEXTBOOK OF INORGANIC CHEMISTRY - VOLUME I, II, III, IV**

**A TEXTBOOK OF PHYSICAL CHEMISTRY - VOLUME I, II, III, IV**

**A TEXTBOOK OF ORGANIC CHEMISTRY - VOLUME I, II, III, IV**

ISBN: 978-81-938720-0-0



9 788193 872000 >

MRP: Rs 800.00

**D** DALAL  
INSTITUTE

Main Market, Sector 14, Rohtak, Haryana 124001, India

(+91-9802825820, [info@dalalinstitute.com](mailto:info@dalalinstitute.com))

[www.dalalinstitute.com](http://www.dalalinstitute.com)