

### ❖ Chelate Effect and Its Thermodynamic Origin

The chelate effect or chelation may simply be defined as an equilibrium reaction between the complexing agent and a metal ion, characterized by the formation of two or more bonds between metal and the complexing agent, resulting in the formation of a ring structure including the metal ion.

The term ‘chelates’ was first proposed by Morgan and Drew in 1920 for the cyclic structure arising from the assembly of metals with organic ligands. The chelate effect results in the enhanced affinity of chelating ligands for a metal ion compared to the affinity of a collection of similar non-chelating monodentate ligands for the same metal. This, in turn, results in the larger values of overall formation constants for the chelate complexes than their monodentate counterparts.



Figure 9. Popular chelating ligands; (a) ethylenediamine (symmetrical) and (b) glycinate (unsymmetrical).

#### ➤ Characteristic Features of Chelates

The Chelate complexes generally have low melting points and are soluble in the organic solvents. Now though the phenomenon of chelation follows pretty much all rules of metal-ligand bonding as followed by simple complexes; two characteristic features of the chelate complexes are unique and can be given as:

**1. Ligand-type:** One of the most obvious features of the chelates is that only polydentate ligands are capable of forming chelate complexes. The ligand can be bidentate, tridentate or even hexa-dentate; but it must have more than one donor sites to form the chelate.

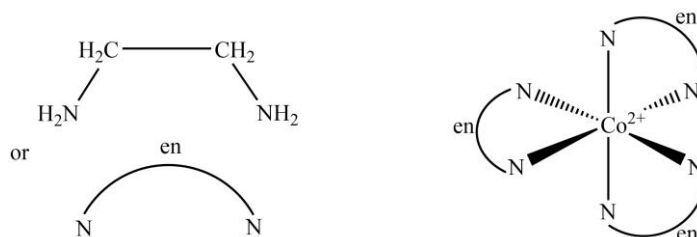


Figure 10. Structure of chelate complex of  $\text{Co}^{2+}$  with the bidentate ligand.

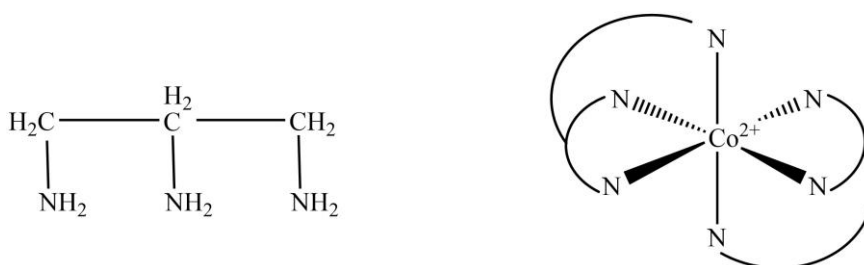
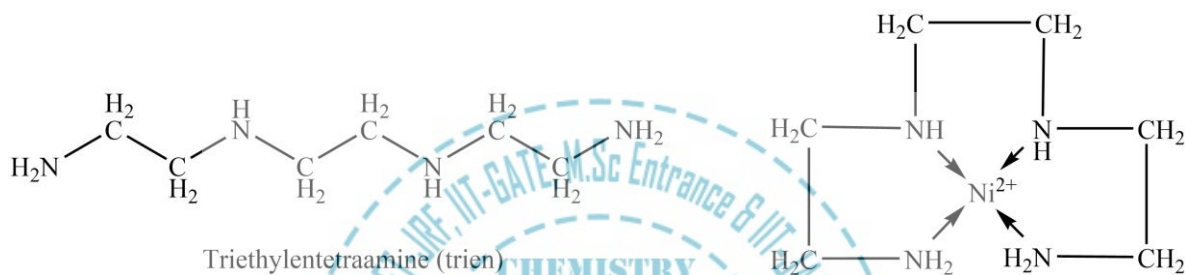
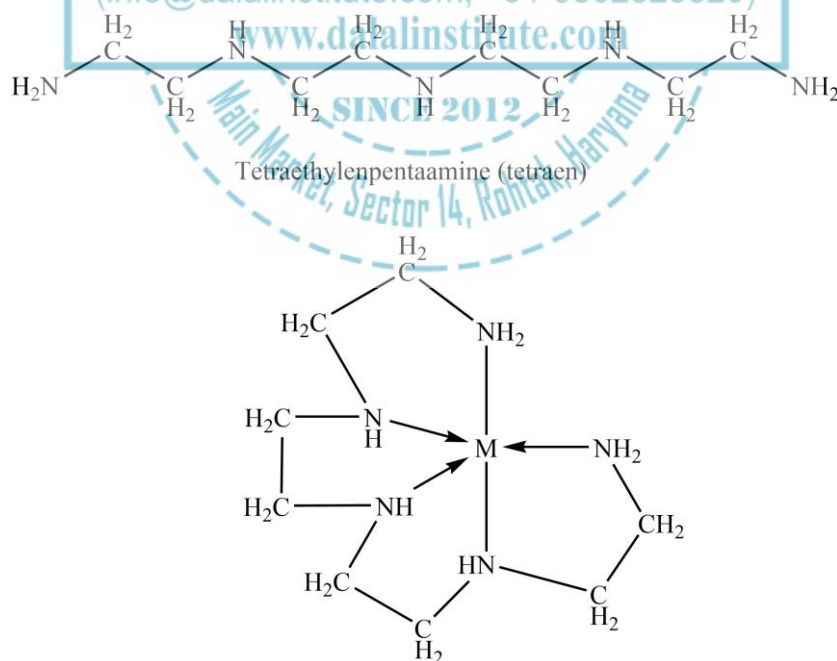
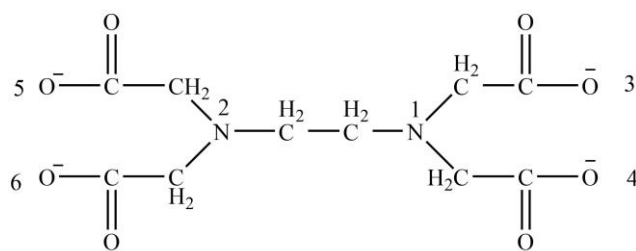
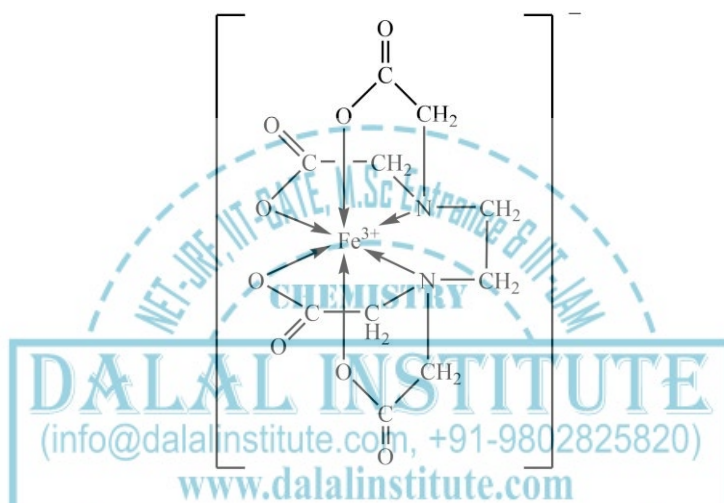
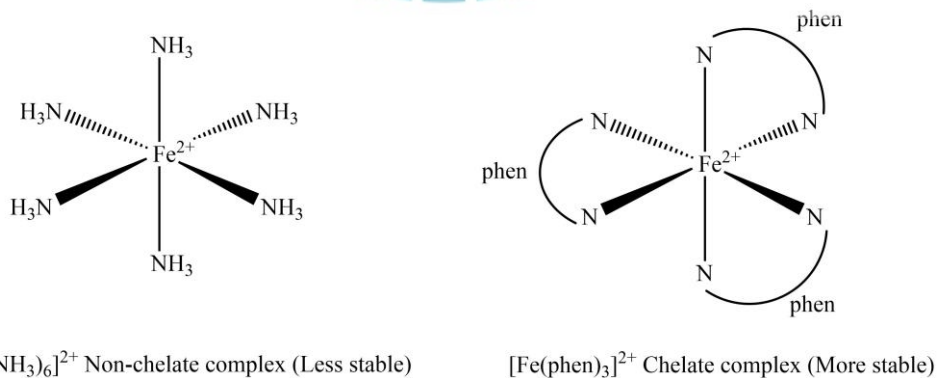
Figure 11. Structure of chelate complex of  $\text{Co}^{2+}$  with a tridentate ligand.Figure 12. Structure of chelate-complex of  $\text{Ni}^{2+}$  with a tetradentate ligand.

Figure 13. Structure of metal chelate-complex with a pentadentate ligand.

Ethylenediaminetetraacetate (EDTA<sup>4-</sup>)Figure 14. Structure of chelate complex of Fe<sup>3+</sup> with hexadentate ligand.

**2. Stability:** The chelating agent binds with the metal-center of suitable size firmly and the bond can be covalent or coordinate. This makes the chelate complexes as more stable than their non-chelating counterparts.

[Fe(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> Non-chelate complex (Less stable)[Fe(phen)<sub>3</sub>]<sup>2+</sup> Chelate complex (More stable)Figure 15. Structure of chelate complex of Fe<sup>2+</sup> with a bidentate ligand.

Also, it has also been observed that five and six-membered ring chelate complexes are more stable than the other due less steric strain. The chelating ligands like ethylenediamine, which do not have multiple bonds, prefer to form five-membered rings complexes; while the chelating ligands like acetylacetonate, which do have double bonds, prefer form six-membered rings complexes.

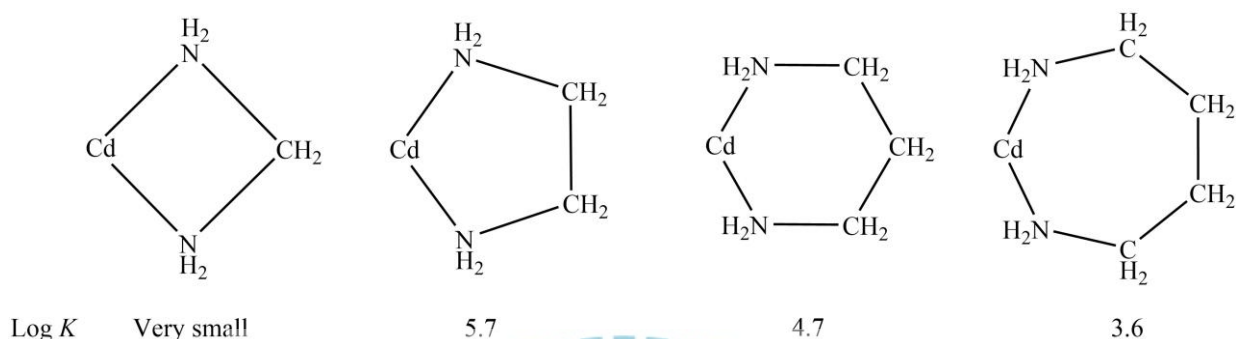


Figure 16. Stability order for the bivalent cadmium complexes of bidentate amines.

Furthermore, the chelating ligands with bulky groups usually form less stable complexes due to the weakening of the metal–ligand bond arising from the steric hindrances. For instance, consider the case of metal complexes involving 2,2-bipyridyl and its derivatives as the chelating ligand. The structures of bivalent iron complexes with normal 2,2-bipyridyl and 4,4'-Dimethyl-2,2'-bipyridyl as the chelating ligand clearly shows that the former has less steric hindrance, and therefore, is more stable.

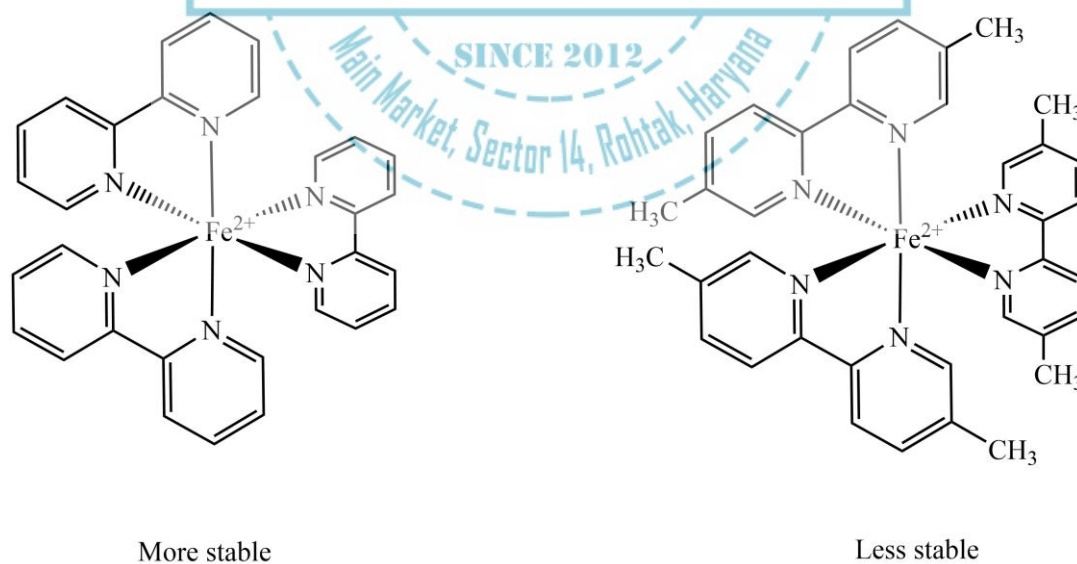


Figure 17. Structures of bivalent iron complexes with normal 2,2-bipyridyl and 4,4'-Dimethyl-2,2'-bipyridyl as the chelating ligand.

➤ **Thermodynamic Explanation of Chelation**

The principal driving force for the chelation phenomena is the stability gain arising from the increasing entropy during the complexation. The free energy change for a general reaction is given by:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{or} \quad \Delta G^\circ = -RT \ln K \quad (39)$$

Now, as the enthalpy change between non-chelate and chelates is almost negligible because of the similar metal–ligand donor type, the free energy change is primarily governed by the value of  $\Delta S^\circ$ . Furthermore, it follows from the equation (39) that  $\Delta G^\circ$  will become more negative with a more positive value of  $\Delta S^\circ$ , which in turn would increase the value of stability constant  $K$ . Hence, the stability of metal complexes increases with chelation as it occurs through an increment in the entropy of the system.



$$1 + 4 = 5 \qquad \qquad \qquad 1 + 4 = 5$$



$$1 + 2 = 3 \qquad \qquad \qquad 1 + 4 = 5$$

Thus, chelation is a thermodynamically favorable process as the number of species in the product are higher than that of what it was in the starting materials leading to enhanced randomness.



$$1 + 1 = 2 \qquad \qquad \qquad 1 + 4 = 5$$

It is obvious that entropy increase in case of trien is higher than ethylenediamine ligand making the trien chelate complex as more stable. The stability of chelate complexes increases with the denticity of the chelating agent.

➤ **Factors Affecting the Stability of Chelate Complexes**

**1. The size of the chelate ring:** Five or six membered chelate rings are more stable than the four, seven, eight or higher membered chelate rings due to less steric strain.

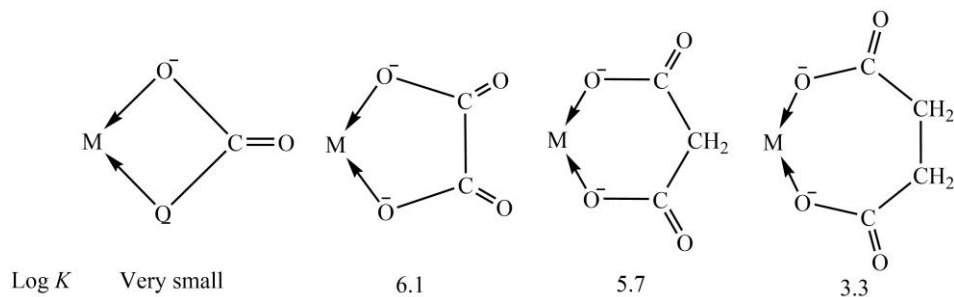


Figure 18. Stability order for the  $\text{Cu}^{2+}$  complexes with chelating ligands.

**2. Number of chelate rings and nature of the metal ion:** it has been observed that as the number of donor sites increase, the stability of metal chelates also increases. Furthermore, the stability of chelate complexes was also found in accordance with the Irving-William series.

Table 3. The values of overall formation constants ( $\log \beta$ ) for different types of metal ions as a function of the number of chelate rings.

Metal complex	No. of chelate rings	Values of overall formation constants ( $\log \beta$ )						
		Mn <sup>2+</sup>	Fe <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>
M(NH <sub>3</sub> ) <sub>4</sub>	0	–	3.7	5.31	7.79	12.59	9.06	6.92
M(en) <sub>2</sub>	2	4.9	7.7	10.9	14.5	20.2	11.2	10.3
M(trien)	3	4.9	7.8	11.0	14.1	20.2	12.1	10.0
M(tren)	3	5.8	8.8	12.8	14.0	18.8	14.6	12.3
M(dien) <sub>2</sub>	4	7.0	10.4	14.1	18.9	21.3	14.4	13.8
M(penten)	5	9.4	11.2	15.8	19.3	22.4	16.2	16.2

In addition to stability prediction by Irving Williams series, transition metal ions usually form more stable chelate complexes and follow the order given by Maley and Mellor.



**3. Resonance effect:** The resonance stabilization of the chelate ring also enhances complex stability. For example, the exceptionally high  $\log \beta$  for [Fe(acac)<sub>3</sub>] is due to resonance stabilization in the chelating ligand.

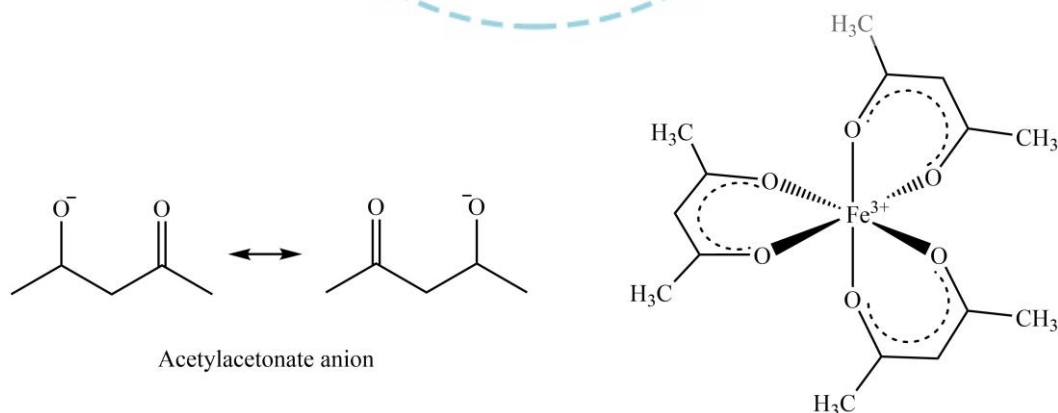


Figure 19. The resonance stabilization in tris(acetylacetonato) iron(III) or [Fe(acac)<sub>3</sub>].

**4. Lewis base strength and charge of ligand:** Calvin and Wilson studied the  $\text{Cu}^{2+}$  chelate complexes and proved that the stability of the chelate complexes increases with the increase of the basic character of the ligand. Moreover, it has also been observed that the uncharged ligands like ethylenediamine or triethylenetetraamine form more stable complexes than the anionic ligands like oxalato or glycinate.

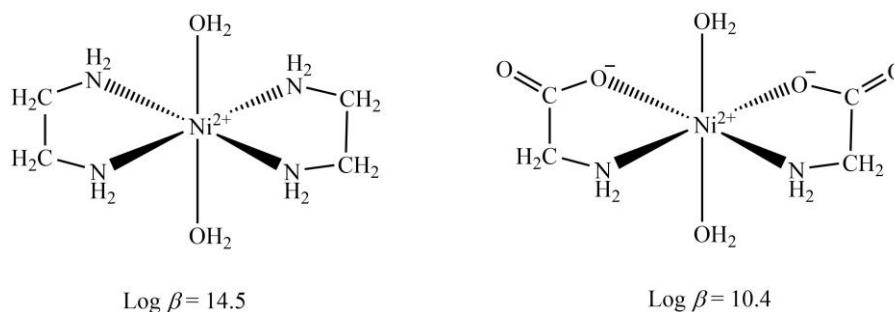


Figure 20. Stability order for the  $\text{Ni}^{2+}$  complexes with neutral and anionic chelating ligands.

**5. Steric hindrance and strain due to large ligands:** The chelating ligands with large groups usually form less stable complexes due to the weakening of the metal–ligand bond arising from the steric hindrances. For example, ethylenediamine form more stable complexes with bivalent metal ions than N-tetramethylethylenediamine, which obviously due to greater steric hindrance in the later one. Moreover, the overall stability can also be affected by the strain in metal–chelates arising from the particular geometry of the chelating ligand. For instance, trien-complexes of bivalent copper are more stable than their tren-complexes due to less steric strain as trien-ligand can adapt square planar coordination much easily.

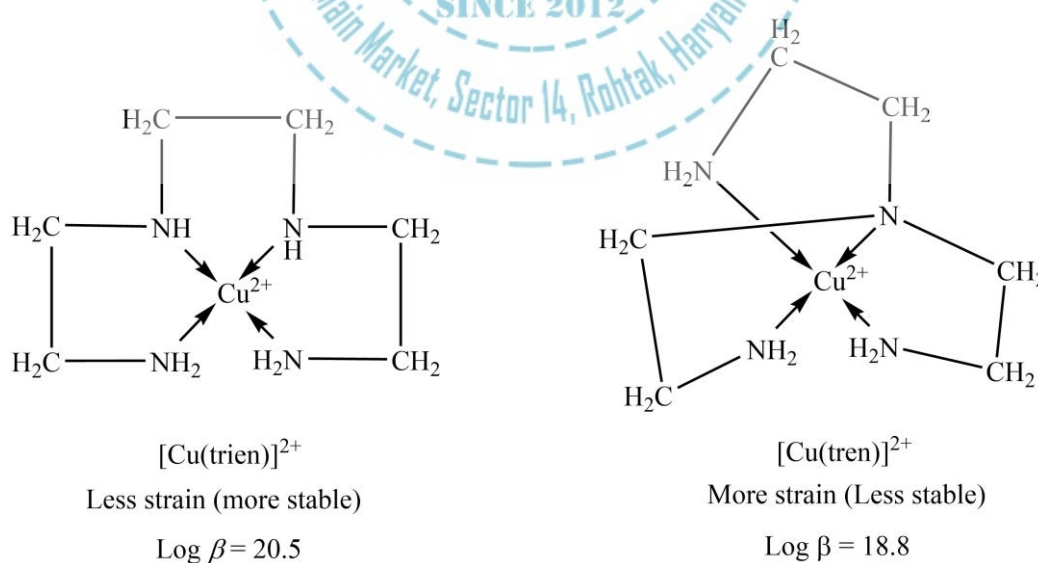


Figure 21. Stability order for the  $\text{Cu}^{2+}$  complexes with chelating ligands.

➤ *Main Applications of Chelates*

1. The colored chelate complex formation with  $\text{Al}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mg}^{2+}$  can be used to quantify these metals from their solutions.
2. The hardness of water can be removed by synthesizing the water-soluble chelate complexes of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ion which otherwise undergoes precipitations reaction.
3. Some neutral chelate complexes are sparingly soluble in water but have high solubility in an organic solvent that can be used to purify metal in the organic phase.
4. The chelating agents like EDTA can be used to eliminate harmful radioactive metal from the body forming their water-soluble complexes.
5. Chelating agents can also act food preservatives by binding or sequestering metal ions like iron or copper in certain foods in order to prevent the metals from oxidizing and speeding up spoilage.



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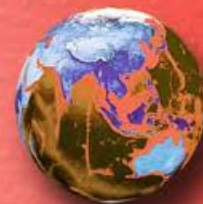
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# A TEXTBOOK OF INORGANIC CHEMISTRY

**Volume I**

**MANDEEP DALAL**



*First Edition*

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# 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>



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