



E-NOTE FOR INSTRUCTIONAL DELIVERY
AL-HIKMAH UNIVERSITY, ILORIN, NIGERIA

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AL-HIKMAH UNIVERSITY, ILORIN, NIGERIA
Adeta Road, Adewole Housing Estate, P.M.B. 1601, Ilorin
.....learning for wisdom and morality.....
CENTRE FOR ICT AND DISTANCE LEARNING (IDL)
e-CONTENT DEVELOPMENT (DL) UNIT

A. Course Lecturer's Detail

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B. Faculty, Department and Programme

Faculty: Education

Department: Science Education

Programme: Chemistry Education

C. Course Title: Coordination Chemistry

D. Course Code: CHM 415

E. Course Credit: 2

F. Course Description: Introduction and Application of Coordination Compounds; Nomenclature and Isomerism in complexes; Theories of Structure and Bonding; Physical Methods of Structural Investigation; The Spectrochemical Series, The Nephelauxetic Series and Jahn Teller's Effect; Thermodynamics of Complexes.

G. Learning Objective: At the completion of this e-note, it is expected that learners will achieve the following:

1. Describe the concept of coordination chemistry and its applications
2. Explain the theories and physical methods of investigating coordination compounds structure.
3. Apply spectrochemical series, nephelauxetic series and Jahn-Teller's effect in describing nature, formation and structural features of coordination complexes.
4. Describe the thermodynamics of coordination complexes.
5. Design the synthesis and explain mechanism of coordination complexes formation.

H. Notes on Course Outline (Topics to be taught)

Introduction and Application of Coordination Compounds

Coordination chemistry is the chemistry of Lewis acid-base adduct, Lewis acids are characterized with tendency to accept at least a lone pair of electrons while Lewis base usually have at least one lone pair of electrons to share. The Lewis acids and bases when interact chemically form a coordination covalent bond by sharing the pair of electrons from the base. Transition metals generally serve as Lewis acids due to the possession of at least one vacant low lying orbital (3d, 4d orbitals) which can readily accept a lone pair of electron from a ligand, the Lewis base. The study of coordination chemistry is also extended to compounds of metal-carbon bonds, organometallic compounds.

The ligands can be classified as monodentate, bidentate, tridentate and polydentate based on the number of lone pair electrons that can coordinate. Example of monodentate is NH_3 , CN^- ; bidentate: ethylenediamine, bipyridine aminoethanethiolate ion, $\text{NH}_2\text{CH}_2\text{CH}_2\text{S}^-$; Tridentate: diethylenetriamine and polydentate: ethylenediaminetetracetate ion (EDTA).

valences, where the charge of the positive metal ion is satisfied by that of the negatively charged ion. The secondary valency can be satisfied by negative, positive or neutral group and are usually equals the coordination number. Coordination number is the number of coordinate covalent bonds towards the central metal in a complex. Coordination number is one of the factors that determine the geometry and symmetry of coordination compounds. It was Werner's theory that clarifies the fact that coordination compounds are special class of compounds unlike the ionic, covalent compounds and the molecules.

Complex	Primary Valency	Secondary Valency
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	3	6
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	2	6
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	1	6

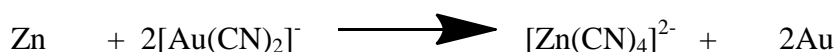
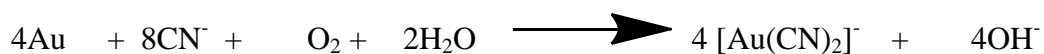
Measurement of conductivity and stoichiometric precipitation reaction with acidified silver nitrate solution was used to established primary valency. The common coordination number for metal complexes are 2, 4 and 6, though other oxidation state do exist.

Name	Formula	Coordination Number	Geometry
Silverdiamine	$[\text{Ag}(\text{NH}_3)_2]^+$	2	Linear
Diaminedichloroplatinum II	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	4	Square planar
Copper II tetraamine	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	4	Tetrahedral
Tris(ethylenediamine)cobalt III	$[\text{Co}(\text{en})_3]^+$	6	Octahedral
Hexacyanoferrate III	$[\text{Fe}(\text{CN})_6]^{3-}$	6	Octahedral

The ligands in the above complexes are said to be in coordination sphere, not as primary valency.

Coordination complexes are applied as catalyst, Ziegler-Natta catalyst TiCl_3 and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, or TiCl_4 with $\text{Al}(\text{C}_2\text{H}_5)_3$. The organoaluminium (triethylaluminium) serves as co-catalyst that enhances the catalytic activity of the olefin polymerization. Rhodium(I) complexes

are also used as catalyst in the isomerization of alkenes. In the extraction and purification of metals, coordination complexes are also of importance. In the extraction of gold from its ores, the aqueous cyanide solution in the presence of air and water forms the complex, cyanoaurate (I) $[\text{Au}(\text{CN})_2]^-$, Which is further reacted with zinc to give pure extracted gold and another complex of zinc is also formed.



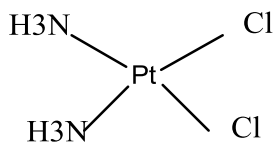
In medicine , EDTA forms very stable complexes with toxic metals to solve the problem of metal poisoning, cis-diaminedichloroplatinum II, cisplatin is one of the prominent drugs in treating cancerous cells. Sodium nitroprusside, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ complex, is a potent vasodilation agent which is important in lowering blood pressure during surgery. The complex can be broken down by hemoglobin into cyanide, which is in part detoxified by liver and kidney to thiocyanate.

Nomenclature and Isomerism in Coordination Complexes

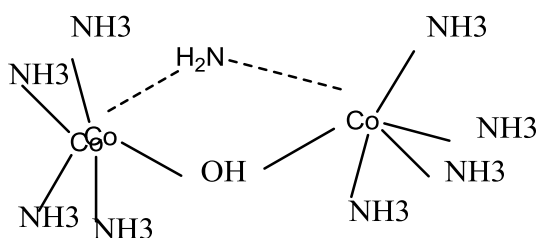
According to IUPAC recommendation on naming coordination compounds, the following rules are applicable to the systematic naming system:

1. Positive ions are named first in complexes before the negative ions, e.g $\text{K}_3[\text{Fe}(\text{CN})_6]$, the potassium ion is regarded as the positive ion and named first, set of elements in the coordination sphere is regarded as the negative ion and named next based on some other rules to stated later. $\text{K}_3[\text{Fe}(\text{CN})_6]$: Potassium hexacyanoferrate (III).
2. Within the coordination sphere that form positive ion, the ligands are named first before the metal, e.g: $[\text{Cu}(\text{NH}_3)_4] \text{SO}_4$: Tetraammine copper (II) sulphate.

3. a. The number of ligands is indicated by the following prefixes: 2- di, 3- tri, 4- tetra, 5- penta, 6- hexa, 7- hepta, 8- octa, 9- nona, 10- deca, etc. Example: $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$ – hexaammine cobalt(III) chloride
- b. If the name of the ligand has already include a prefix, e.g ethylenediammine, (prefix, di, already included), or the name is complicated, the name is set of in parenthesis and the second set of prefixes indicating number of ligand ends in – is/kis, e.g bis- 2, tris- 3, tetrakis- 4, pentakis- 5, hexakis- 6, heptakis- 7, octakis- 8, nonakis- 9, decakis- 10 etc. $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]^+$ - Dichlorobis(ethylenediammine)cobalt(III) ion.
 $[\text{Fe}(\text{NH}_4\text{C}_5\text{-C}_5\text{H}_4\text{N})_3]^{2+}$ - Tris(bipyridine) Iron(II)ion.
4. In a case of more than one ligand in coordination sphere, the ligands should name alphabetically regardless of the prefixes, e.g $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ - Tetraammine dichloro cobalt (III) ion; $[\text{Pt}(\text{NH}_3)\text{Br}(\text{CH}_3\text{NH}_2)\text{Cl}]$ - Amminebromochloromethylamine platinum (II).
5. Anionic ligands are given the suffix, - o -, e.g chloro, bromo, iodo, etc. coordinated water molecule is named, aqua, coordinated ammonia molecule, ammine(double, m)in case of uncoordinated ammonia, single , m is used, e.g methylamine.
6. If the coordination sphere is having overall negative charge, the name of the metal in the sphere is modified to end in –ate, e.g $[\text{PtCl}_6]^{2-}$ - hexachloroplatinate (IV).
7. Oxidation state of metals are indicated by Roman numeral in parenthesis according to Stock system.
8. Oxidation state of metals are indicated by putting overall charges on the coordination sphere in parenthesis after the name of the metal, $[\text{Pt}(\text{NH}_3)_4]^{2+}$ -- tetraammine platinum(+2), this is based on Ewing-Bassett system.
9. To indicate geometrical adjacent and opposite locations, the prefixes; cis and trans are applied, e.g cis- diamminedichloroplatinum(II), cisplatin



10. Bridging ligands between two metals ions have the prefix- μ . E.g



μ -amido- μ -hydroxobis(tetraamminecobaltIV).

11. Naming of some metals takes the origin with modification and ends with the suffix ---ate , provided the complex is negatively charged ,e.g, Gold(Au)- *aurate*, Silver(Ag)-*argentate*, Iron(Fe)- *Ferrate*, etc. $[\text{Au}(\text{CN})_2]^-$ - Dicyanoaurate(I) ion, $[\text{FeCl}_4]^-$ - Tetrachloroferrate(III) ion.

S/N	NAME	FORMULA	STRUCTURE
1	Ethylenediammine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	 ethylenediammine
2	Bipyridine	$\text{NH}_4\text{C}_5\text{-C}_5\text{H}_4\text{N}$	 bipyridine
3	Methylamine	CH_3NH_2	 methylamine
4	Chloro	Cl	 Cl

5	Bromo	Br	—Br
6	Iodo	I	—I
7	Cyano	CN	—C≡N
8	Hydroxo	OH	—OH
9	Amido	NH ₂	
10	Ammine	NH ₃	
11	Aqua	H ₂ O	

Isomerism in Coordination Complexes

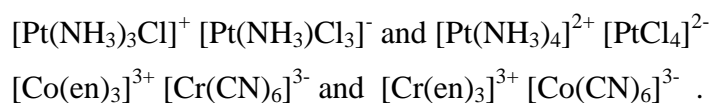
- a. Constitutional Isomerism
 - i. Hydration Isomers
 - ii. Coordination Isomers
 - iii. Ionization Isomers
 - iv. Linkage Isomers
- b. Stereoisomerism
 - i. Geometrical Isomers
 - ii. Optical Isomers

Hydration Isomers: The number of water molecules acting as ligands in the complexes differ though the complexes possess similar molecular formula. This is as a result of interchange of water molecule and another ligand within and outside coordination sphere. The compound with molecular formula, CrCl₃.6H₂O, has the following isomers with different colour:

- [Cr (H₂O)₆] Cl₃ Violet colour
- [Cr Cl(H₂O)₅] Cl₂. H₂O Blue- Green colour
- [Cr Cl₂(H₂O)₄] Cl. 2H₂O Dark Green colour
- [Cr Cl₃(H₂O)₆] . 3H₂O Yellow -Green colour

The isomerism can also be regarded as solvent isomerism if solvent molecule like NH_3 is used as precipitating agent.

Coordination Isomers: At least two metal ions form the complex but ligands coordinated to specific metal ion differ for the two complexes that form the isomers. This implies that the compound has cation has a complex ion and the anion also as complex ion, the ligands of the cation and that of anion are technically exchanged. The ligand- metal ratio remains the same. Example:



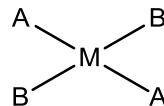
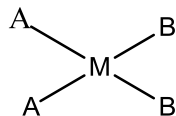
Ionization Isomers: Isomers are characterized with a kind of exchange between anion within inner coordination sphere and those outside the coordination sphere. If the complex is dissolved in water for example, the number of anion outside the coordination sphere can be detected. The three complexes listed below are ionization isomers:

- $[\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]\text{SCN}$
- $[\text{Co}(\text{en})_2(\text{NO}_2)\text{SCN}]\text{Cl}$, Cl is exchanged for SCN
- $[\text{Co}(\text{en})_2(\text{SCN})\text{Cl}]\text{NO}_2$ NO_2 is exchanged for SCN

Linkage Isomers: The ligands that form the complexes usually have more than one donor atom for coordination, such ligand can therefore coordinate the central metal ion in more than one way. Thiocyanate ion, SCN^- and Nitro group, NO_2 are examples of such ligands.

- $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ coordination via N-atom
- $[\text{Co}(\text{NH}_3)_5\text{SCN}]^{2+}$ coordination via S-atom

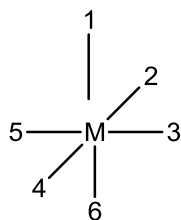
Geometrical Isomers: Square planar geometry complexes of the formula, MA_2B_2 can form cis-trans isomers. Octahedral complexes of the formula, MA_4B_2 also show cis-trans isomerism.



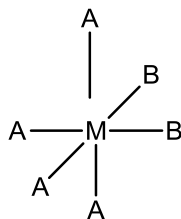
Cis- form (square planar)

trans- form (square planar)

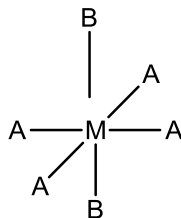
The compound , $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ can form any of the isomers above.



General ligand position on octahedral structure



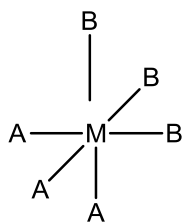
Cis- form (Ligand B, on position, 2 and 3)



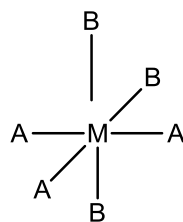
trans- form (Ligand B, on position, 1 and 6)

The complex, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$ having octahedral geometry can show either cis or trans isomerism as describe above.

Octahedral complexes of the formula MA_3B_3 exhibit meridional(mer) or facial(fac) isomerism. In fac- isomers, the B ligands are placed on the position, 1, 2 and 3, while in mer- isomers they are positioned on 1, 2, and 6.



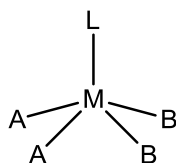
Fac- form



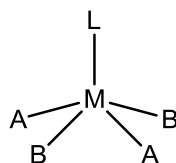
mer- form

The complex, $[Co(NH_3)_3Cl_3]$ shows mer or fac isomerism.

Complexes of square based pyramidal structure of the formula, MLA_2B_2 can also show cis-trans isomerism.

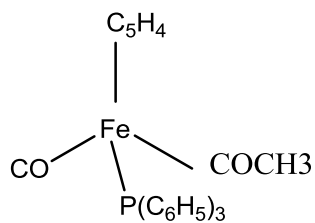


Cis- form

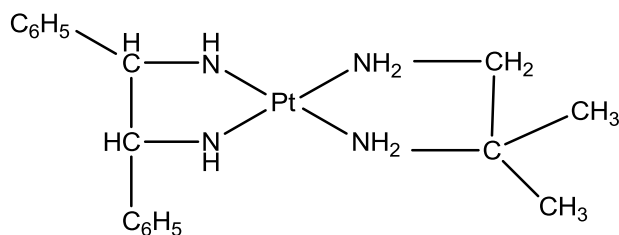


trans- form

Optical Isomers: The complexes are characterized with non-superimposable mirror images, no line of symmetry/plane of symmetry and presence of chiral centre. The molecular complexes exhibiting optical isomerism will rotate plane polarized light clockwise (dextrorotatory) or anticlockwise (laevo-rotatory). Tetrahedral complexes of the formula, $MLABC$ will show optical isomerism since the ligands are unsymmetrical.

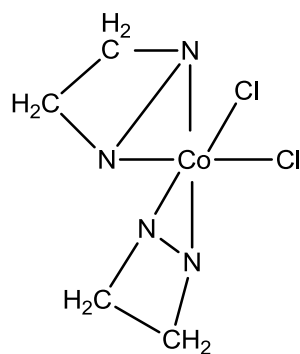


{Tetrahedral: Chiral centre}



Meso-stilbenediamine(iso-butylendiamine)platinum
unsymmetrical}

II {Square planar:



Cis- dichlorobis(ethylenediamine) cobaltII { Octahedral: No plane of symmetry}

Note : Superimposability as a result of rotation via 180°

Theories of Structure and Bonding in Coordination Complexes

- Electrostatic Theory

- Valence Bond Theory
- Crystal Field Theory
- Ligand Field Theory

NOTE: *The theories will be discussed with reference to octahedral structure complexes*

- **Electrostatic Theory:** The theory assumes that ligands which are negatively charged approach the positively charged central transitional metal ion. The two chemical species attract each other electrostatically and combine the coordination complexes; the ligands also repel each other. Based on the repulsion between the ligands, complexes with coordination number of two will be linear, 3- trigonal planar, 4-tetrahedral, 6-octahedral etc.
- The theory cannot explain the existence of complexes with neutral ligands (CO, NH₃, H₂O etc) and the existence of square planar complexes. Some other properties of metal complexes such as magnetic properties, colour and spectra cannot be explain by this theory.
- **Valence Bond Theory :** Considering first row transition elements for example, the s, p and two of the d- orbitals ($d_{x^2-y^2}$, d_z^2) undergo hybridization forming six- hybrid orbitals, (sp^3d^2 (4d orbitals are used) or d^2sp^3 (3d orbitals are used). The six hybrid orbitals are positioned at the vertices of an octahedron.
- The hybrid orbitals can combine with various orbitals from the ligand(s), making bonding and antibonding orbitals, each with σ symmetry around the metal- ligand bond axis.
- After the overlapping, each of the lone pair electrons from ligands are shared with metal ion using the bonding molecular orbital as coordinate covalent bonds is formed.
- Outer - orbital sp^3d^2 complexes: 4s, 4p and two of the 4d orbitals are hybridized. Structurally in this type of complexes, the d-orbitals lie above the s and the p- orbitals.

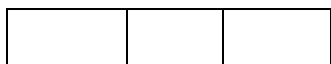
Example of such complexes is CoF_6^- . The Co^{3+} has the electronic configuration, $[\text{Ar}] 3d^6$ and the distribution is as given below



$3d^6$



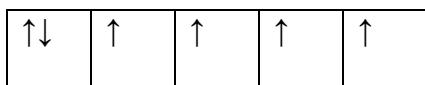
$4s$



$4p$

Note: In the 4^{th} shell there also exist the $4d$ sub-shell, for the outer -orbital complexes, it is the two of the five $4d$ orbitals that hybridized with the $4s$ and $4p$ orbitals.

For ligands forming octahedral complex with this metal ion, six coordinate covalent bonds are formed using the six hybrid orbitals, sp^3d^2 ($4s$, 3 of the $4p$ and 2 of the $4d$ -orbitals.). The complex CoF_6^- is therefore paramagnetic considering the structure below.

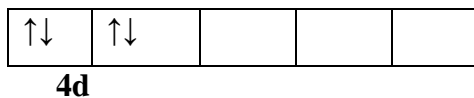
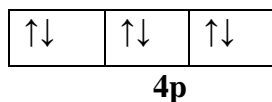


$3d^6$

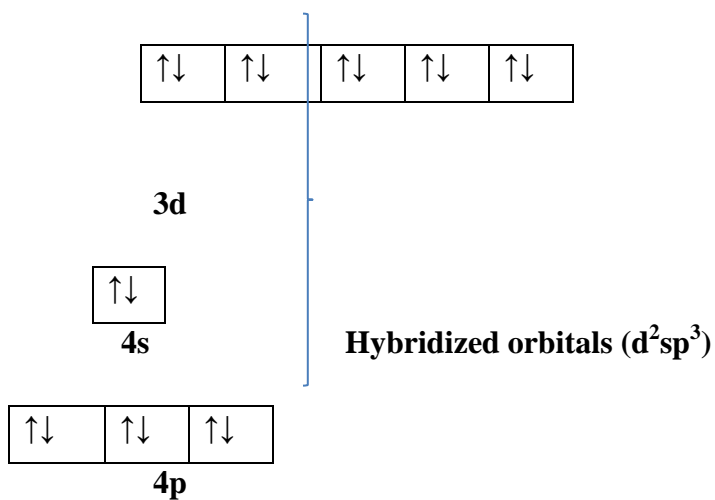


$4s$

Hybridized orbitals (sp^3d^2)




- Inner- orbital complexes are formed when two of the 3d-orbitals hybridized with 4s and 4p orbitals forming the 6-hybrid orbitals. Ligands such as CN^- , CO tend to form inner orbital complexes. The six electrons in the 3d sub-shell of the Co^{3+} are distributed between three of the 3d-orbitals and the other two 3d-orbitals are hybridized with 4s and the 4p orbitals.

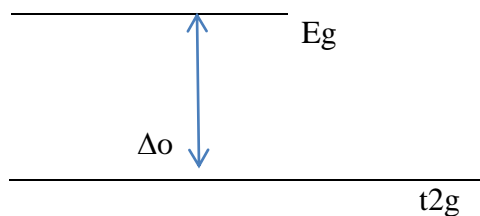


Note: 6 monodentate ligands are expected to share 6 lone pairs of electrons with metal ion

The complex such as $\text{Co}(\text{NH}_3)^{3+}$ that is inner-orbital is therefore diamagnetic.

- The valence bond theory can therefore explain magnetic properties of metal complexes.

- **Crystal Field Theory:** By geometry, d_{xy} , d_{xz} and d_{yz} orbitals have lower energy compared to the $d_{x^2-y^2}$, d_z^2 orbitals. When lone pair electrons from ligands are closer to the d-electrons of the metal ion, electrostatic repulsion occurs, degree of which depends on the geometry of the d-orbitals. $d_{x^2-y^2}$, d_z^2 orbitals are mostly affected compared to the d_{xy} , d_{xz} and d_{yz} . The electrons in the d_{xy} , d_{xz} and d_{yz} orbitals are more stable.
- The net result of the electrostatic interaction is that the five d-orbitals are split into two energy levels, the lower t_{2g} and the upper e_g , separated by a crystal field splitting energy, Δ_o . The crystal field splitting energy, Δ_o is a measure of the energy absorbed when one electron is promoted from the t_{2g} level to the e_g level.
- Depending on the size of Δ_o , ligands can be classified as strong field or weak field ligands, some are said to be intermediate. A smaller value of Δ_o implies that a metal ion having more than three electrons in the d-subshell will distribute the electrons between the t_{2g} level and the e_g , while a higher value of Δ_o indicates that electrons will be paired at the t_{2g} level before being distributed at the e_g level.
- CO, CN⁻, en, NH₃, NCS, H₂O, OH⁻, F⁻, Cl⁻,

- Consider the two complexes, CoF_6^- and $[\text{Co}(\text{NH}_3)_6]^{3+}$. The first complex, the ligand is weak field (high spin) and the six electrons in the metal ion spread out among the five d-orbitals since Δ_o is smaller for this type of ligand, and the complex is therefore paramagnetic (Fig 1)



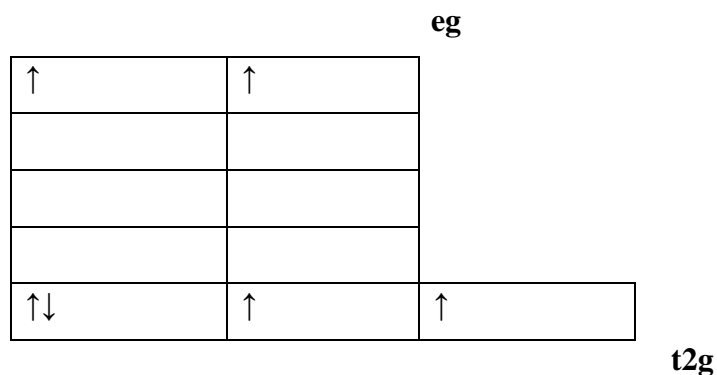


fig. 1

For the second complex, the ligand is a strong field ligand (low spin) and the Δ_o value is higher therefore the six electrons from the central metal ion are distributed between the orbitals in the t_{2g} level and the complex is therefore said to be diamagnetic, fig 2.

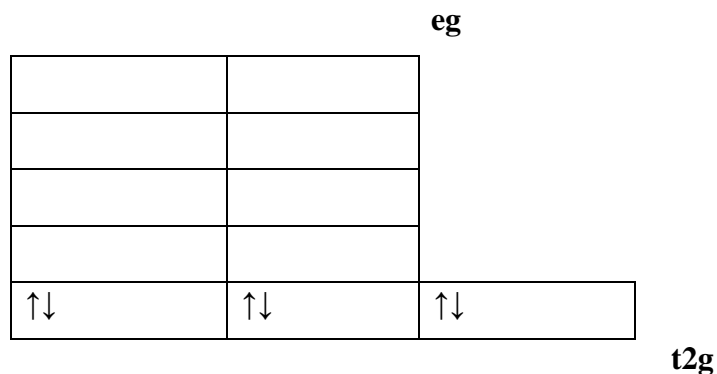


fig. 2

Ligand Field Theory: The ligand-field model for an octahedral transition-metal complex such as $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion assumes that the $3d(d_{x^2-y^2}, d_z^2)$ orbitals, $4s$, and $4p$ orbitals on the metal overlap with one orbital on each of the six ligands to form a total of 15 molecular orbitals (5 from $3d$, 1 from $4s$, 3 from $4p$ and 6 from the ligands). This is possible because ligand orbitals for

octahedral complexes have σ –symmetry around the metal – ligand bond lines. The fifteen molecular orbitals so formed are shown below with respective notation.

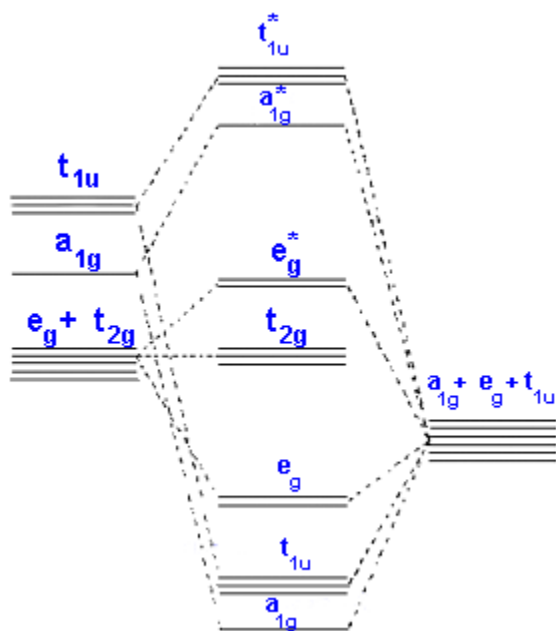


Fig. 3: The 15 molecular orbitals and their notations

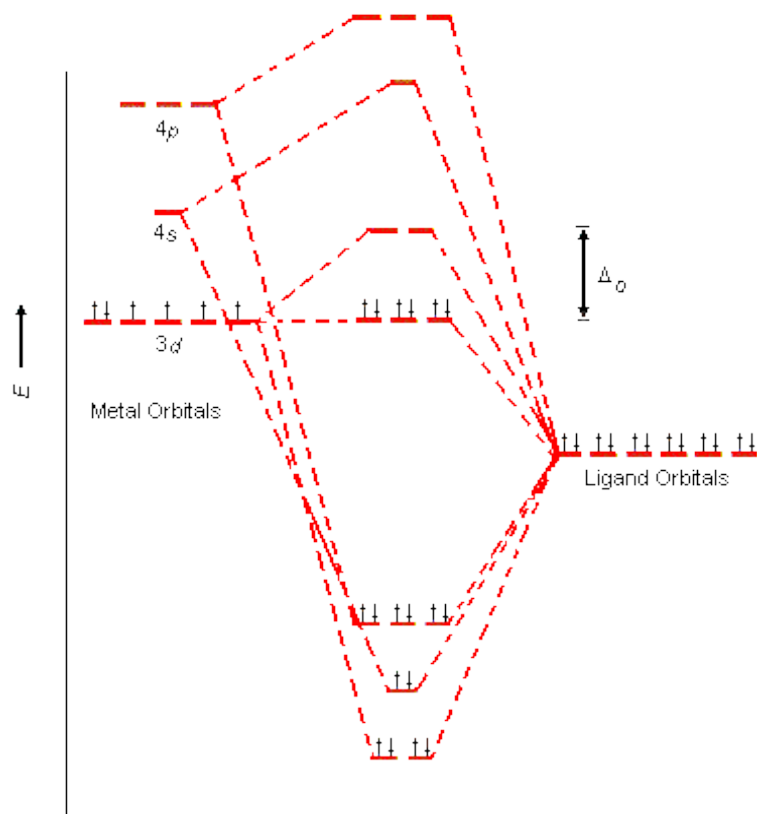
Six of these orbitals are *bonding molecular orbitals*, whose energies are much lower than those of the original atomic orbitals. Another six are *antibonding molecular orbitals*, whose energies are higher than those of the original atomic orbitals. Three are best described as *nonbonding molecular orbitals*, because they have essentially the same energy as the 3d atomic orbitals on the metal.

Note

<i>Bonding molecular orbitals</i>	$[a_{1g}(2), t_{1u}(1), e_g(3), \text{sub total of six}]$	} The fifteen molecular orbitals
<i>Nonbonding molecular orbitals</i>	$[t_{2g}(3), \text{sub-total of three}]$	
<i>Antibonding molecular orbitals</i>	$[e_g^*(2), a_{1g}^*(1), t_{1u}^*(3), \text{a sub-total of six}]$	
<i>3d orbitals notation</i>	- t_{2g}, e_g	
<i>4s orbital notation</i>	- a_{1g}	

4p orbitals notation - t_{1u}

Consider the complex ion, $[\text{Co}(\text{NH}_3)_6]^{3+}$, the ligand, NH_3 each possessing a lone pair of electron (2-electrons each), with the six of the ligands contributing a sub-total of 12 electrons. The metal ion, Co^{3+} has 6-electrons. The total number of available electrons for distribution among the molecular orbitals is 18. This is used to give the molecular diagram.



- **Spectrochemical Series:** List of ligands from the strong π - acceptor effect ligands to the strong π -donor effect ligands. It shows the order of the ligand field split energy, Δ of the ligands. A summary of the list is as given below:
- $\text{CO}, \text{CN}^- > \text{phen} > \text{NO}_2^- > \text{en} > \text{NH}_3 > \text{NCS}^- > \text{H}_2\text{O} > \text{F}^- > \text{RCO}_2^- > \text{OH}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

- CO, CN⁻, phen, NO₂⁻ show the possibility of π- back bonding due to the possession of vacant π* or d-orbitals and are generally referred as π- acceptors.
- Ligands such as H₂O, F⁻, OH⁻, RCO₂⁻.... have occupied p-orbitals and are potentially π-donor ligands. They tend to donate the electrons in the p-orbitals to the metals along with the σ-bonding electrons.
- Ligand such as NH₃, en, are σ-donor, and do this only with orbitals of appropriate symmetry for π- interactions. Ethylenediamine, en, has stronger effect compare to NH₃ in terms of ligand field splitting.
- In summary, the π-acceptor ligands are characterized with low spin, strong field and large ligand field split energy, Δ. The reverse is the case for the π-donor ligands while the σ-donor ligands are intermediate.

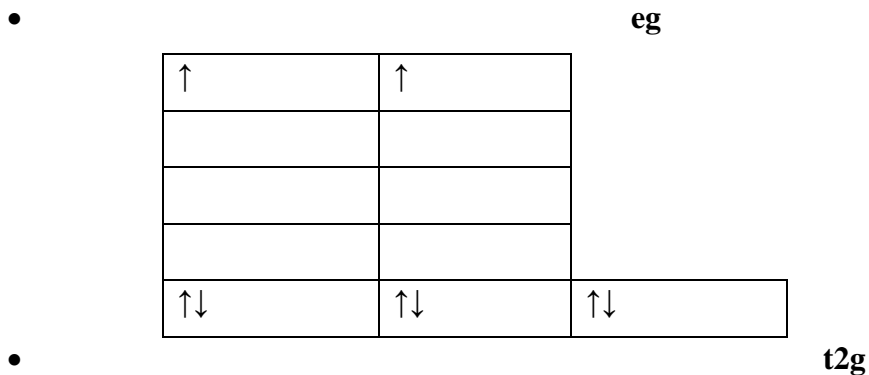
- **Nephelauxetic Series and Effect**

- When ligands bind with metal ion, the orbitals of the metal ion smeared out over a larger region of space i.e the electrons become more delocalized in the complex than they are in the free metal ion. The expansion of the electron cloud is known as the nephelauxetic effect.
- As a result of nephelauxetic effect, the energy required to force pairing electrons in the metal ion complex is therefore smaller than required for the free metal ion.
- The nephelauxetic ratio, β, can be given as the ratio of the Racah parameter, B for metal ion in the complex compare to that in the free state.

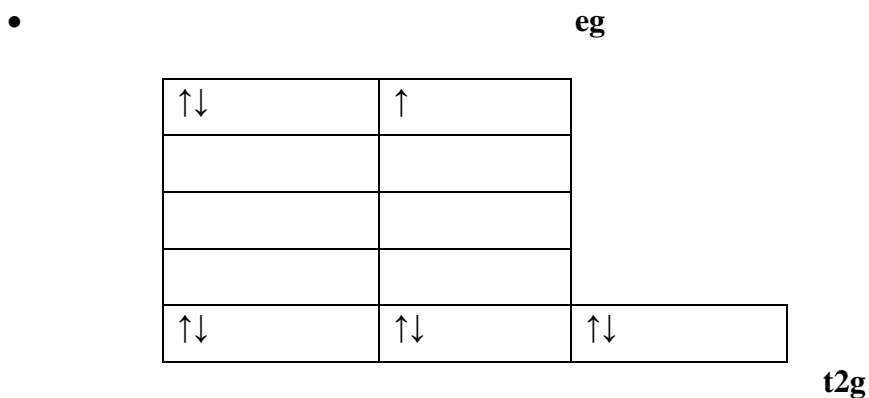
$$\beta = B' / B, \quad B' = \text{Racah parameter for metal ion in complex,}$$

B = Racah parameter for free metal ion

- Based on nephelauxetic parameter for metal ions, the nephelauxetic series is as given below:
- $\text{Ni}^{4+} > \text{Pd}^{4+} > \text{Pt}^{4+} > \text{Mn}^{4+} > \text{Co}^{3+} > \text{Ir}^{3+} > \text{Rh}^{3+} > \text{Fe}^{3+} > \text{Cr}^{3+} > \text{Mo}^{3+} > \text{Ni}^{2+} > \text{V}^{2+} > \text{Mn}^{2+}$
- From the series, nephelauxetic effect is greater for metal ions that are more highly charged, this is because the charge affects the size of the ion making it smaller and highly polarize and the metal ions will therefore experience a greater reduction in interelectronic repulsion by expanding the electron cloud than will a larger metal ion of lower charge.
- A nephelauxetic series for ligands is as given below:
- $\text{I}^- > \text{N}_3^- > \text{Br}^- > \text{CN}^- > \text{Cl}^- > \text{ox}^{2-} > \text{en} > \text{NH}_3 > (\text{CH}_3)_2\text{NCHO} > \text{H}_2\text{O} > \text{F}^-$
- The series indicates that the ability of a ligand to produce nephelauxetic effect decreases as the softness of the ligand decreases and vice-versa. Softer ligands such as Br^- , CN^- , Cl^- , I^- show a greater degree of covalency when bonded to metal ions and they can more effectively delocalized electro density.
- **Jahn-Teller Distortion Effect**
- The Jahn-Teller theorem states that in molecule or ion that have degenerate ground state, the molecule or ion will distort to remove the degeneracy i.e when orbitals in the same level are occupied by different number of electrons, this will lead to the distortion of the molecule. For example, if two orbitals of the e_g level have different number of electrons, this will lead to Jahn-Teller distortion. Cu^{2+} for instance with its d^9 configuration is degenerated and has a J-T distortion but Ni^{2+} with d^8 configuration is high-spin and has one way of filling the e_g level orbitals, therefore not degenerate and exhibit no J-T effect since the e_g level orbitals contain the same number of electrons.

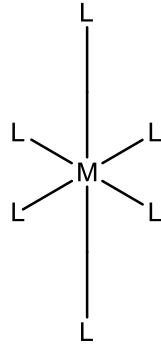


- fig. 5: Ni²⁺ configuration(No distortion)**

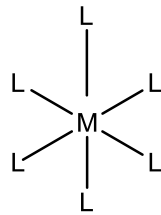


- fig. 6: Cu²⁺ configuration(Showing J-T distortion)**

- For the octahedral complex, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, the six Ni—O bonds are equal in length and have equivalent value of 2.05 Å, while in the complex of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, there are two long axial Cu—O bonds, with values of 2.45 Å and four short in-plane Cu—O bonds with values 2.00 Å, the J-T distortion is responsible for the lengthening of the axial Cu—O bonds. This represents a structural effect of J-T distortion.



- $M = \text{Cu}^{2+}$, $L = \text{H}_2\text{O}$



- $M = \text{Ni}^{2+}$, $L = \text{H}_2\text{O}$

- The J-T distortion also has effect on the splitting of the d- subshell orbitals. According to the crystal field theory, orbitals positioned between axes drop in energy for octahedral complexes (d_{xy} , d_{xz} , d_{yz}) but orbitals d_{z^2} and $d_{x^2-y^2}$ rise in energy on forming complexes due to their geometry.
- For metal ions that have degenerate state, all the d- orbitals with a 'z' in the subscript drop in energy regardless of the geometry, this deviance is due to J-T distortion.
-

$\uparrow\downarrow (d_{z^2})$	$\uparrow (d_{x^2-y^2})$	
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$

t_{2g}

fig 7: Cu^{2+} in regular octahedral environment

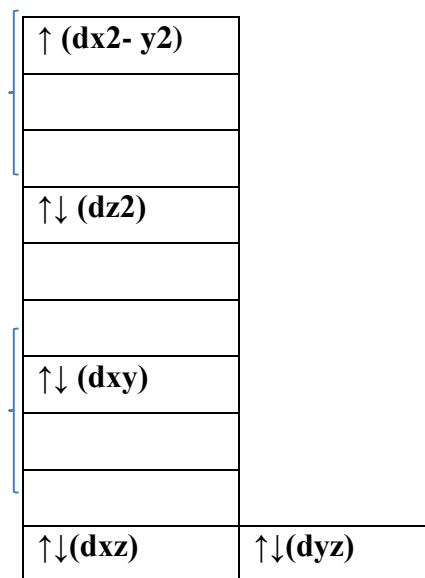


Fig8: Cu²⁺ after J-T distortion

- The arrangement given above for Cu²⁺ (d⁹) configuration is an elongated form of the splitting distortion for octahedral complexes. For d¹ configuration, the reverse is the case and this form is known as compressed form of distortion.
- **Physical Methods of Structural Investigation**

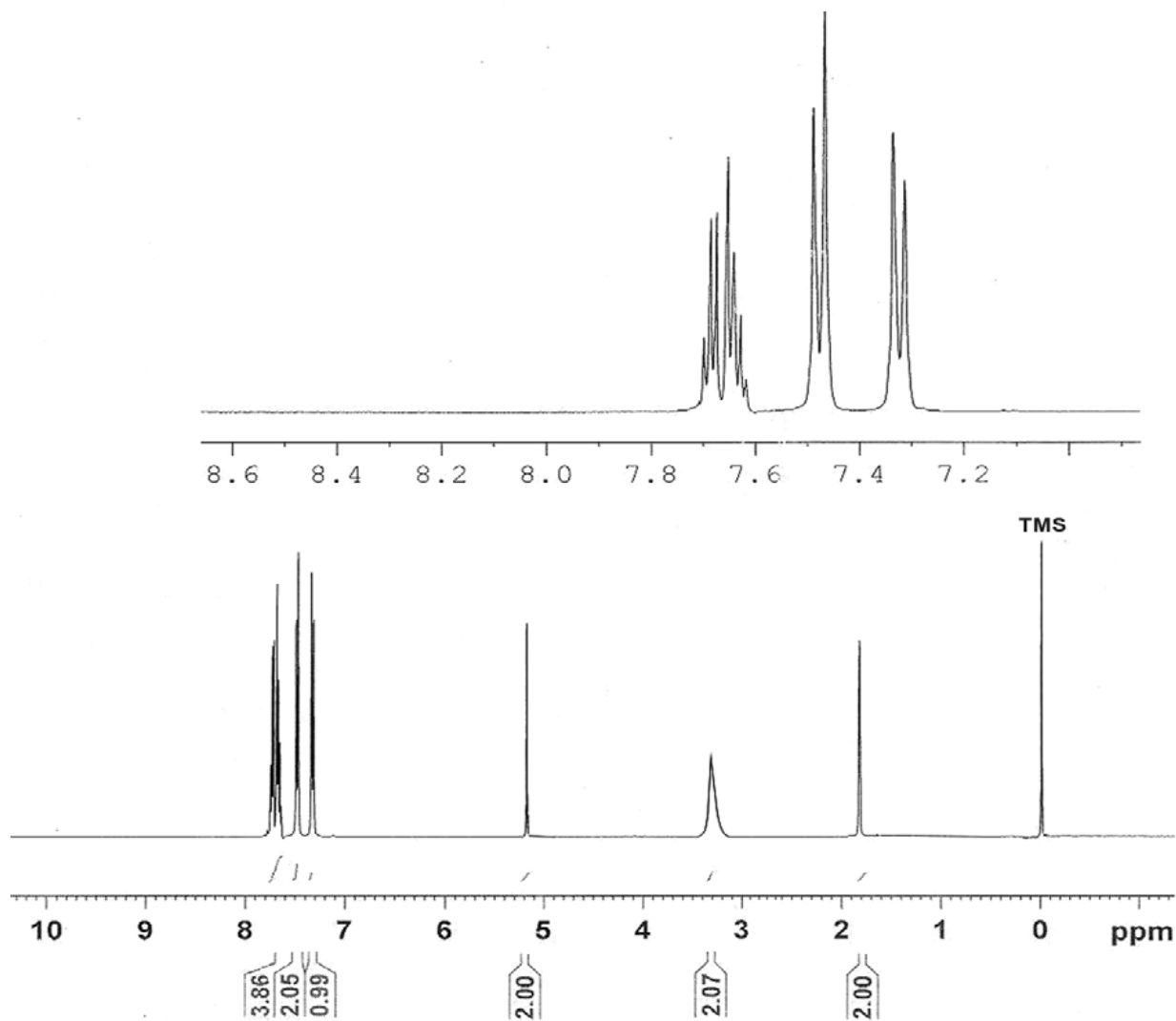
In the structural elucidation of coordination compounds, the following methods are some of the means of identifying the structures:

- Fourier Transform Infrared (FTIR)
- Nuclear Magnetic Resonance (NMR)
- CHN, Elemental Analysis
- X-Ray crystallography

For FTIR analysis, the stretching frequencies of the various interested functional group in the ligands shift in value on coordination with metal ion. The shift in value downfield or upfield

is because of the coordination. The shift in stretching frequency is an indication to the functional group that coordinated. The stretching frequency sometimes disappear indicating the involvement of the given functional group.

In NMR, the magnitudes of the chemical shifts of nuclear resonance in solution are determined by the electron distribution in the molecule or ion containing the nucleus and by the fields set up in the molecule by molecules or ions with which it interacts. Separate resonance bands are observed with magnetically distinct nuclei but a sufficiently rapid chemical exchange between them will result in a single resonance of some intermediate value of chemical shift. The element in the ligand to which the metal ion is coordinated has its signal disappear or shifted in the NMR spectra.



¹H NMR of spectra of Zn(II)–5-FU(A)–val(B) complex

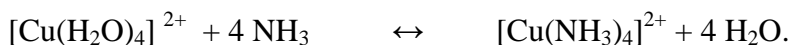
Reference: Sutha et al (2015).

From the spectra above, it is the NMR spectra of mixed metal complex of 5- fluorouracil and the amino acid valine, the nonappearance of proton peak of –COOH for amino acids confirm that gly/ala/val(B) ligands are binded throughout bidentate coordination with the Zn(II) ion via amino –N and deprotonated carboxylato –O atoms. The spectrum of Zn(II) complexes show a characteristic new peak centered between 4.72–4.77 ppm which corroborate the presence of coordinated water molecule in the complexes

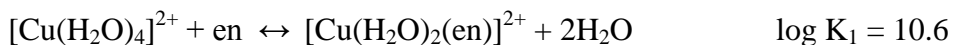
In Elemental analysis, the percentage of C, H, and N found instrumentally in metal complexes and those calculated theoretically are compared and a good agreement suggest the correctness of the proposed molecular stoichiometry of the coordination complex

Thermodynamics of metal complexes

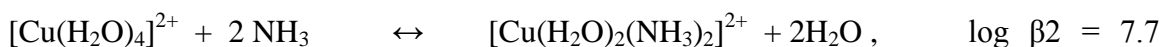
The thermodynamic parameters, ΔG , ΔH and ΔS are related by the equation, $\Delta G = \Delta H - T \Delta S$. In the case of transition metal complexes, the ligand field effects produce contributions most directly related to the enthalpy rather than the free energy changes, this is because ΔH is the property most directly related to the changes in the numbers and strengths of chemical bonds as the system passes from reactants to products. In addition, the magnitude of ΔH may reflect the important steric effects in case of multidentate ligands, consequently multidentate ligands usually produce metal complexes, chelates that are more thermodynamically stable. Thermodynamic stability refers to the change in energy on going from reactants to products, i.e., ΔG for the reaction. Also, $\Delta G = - RT \ln K$, where K is the equilibrium constant for the reaction. Thermodynamic stability often refers to the energetics and associated equilibrium constant for the reaction of an aquated metal ion with some other ligand (other than water).



The stability of the complex of a metal ion with a bidentate ligand such as ethylenediamine (en) is invariably significantly greater than the complex of the same ion with two monodentate ligands of comparable donor ability, for example two ammonia molecule.



$$\Delta H = -54 \text{ kJ mol}^{-1}, \Delta S = 23 \text{ J K}^{-1} \text{ mol}^{-1}$$



$$\Delta H = -46 \text{ kJ mol}^{-1}, \Delta S = -8.4 \text{ J K}^{-1} \text{ mol}^{-1}.$$

This greater stability for complexes of chelate complexes is termed the chelate effect. Its origin is primarily in the differences in entropy between chelate and non-chelate complex reactions. The formation of chelate complexes results in greater disorder because of the formation of a larger number of free particles in the products whereas, there is no change in the number of particles in the formation of comparable nonchelate complexes. The application of EDTA in the treatment of metal poisoning is a justification to the present case and the multidentate EDTA form stable chelate with the poisonous metals such as lead and mercury. In summary, the thermodynamic stability of a metal complex depends on the values of the thermodynamic parameters ΔH , ΔS and the stability constant K and the overall stability constant. (β). In four stepwise substitution reactions, with stability constants, K_1 , K_2 , K_3 and K_4 , the overall stability constant, $\beta = K_1K_2K_3K_4$

Study Questions

1. Explain the term coordination chemistry.
2. How does Werner's theory help to unravel the nature of coordination compounds?
3. Ligands are Lewis bases, discuss the classification of ligands
4. Carboplatin is an analog of the cancer drug, cisplatin, give the coordination number and geometry of carboplatin?
5. Silver can also be extracted by forming coordination complexes, using relevant chemical equation, describe the extraction of silver from its ores *Argentite*?
6. Analyze the type of isomerism in the following metal complexes.
7. Draw the molecular energy diagrams for the following complexes and predict either the complexes are paramagnetic or diamagnetic, give reason.
 - i. $[\text{Fe}(\text{CN})_6]^{3-}$
 - ii. $[\text{Ni}(\text{NH}_3)_6]^{2+}$

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