→ Coordination compounds - Introduction उपसहसंयोजन यौगिक (परिचय) :-

① Simple salt (साधारण लवण) :→

- when an acid reacts with base, neutrilisation takes place and a simple salt is formed.

$$\underset{\text{Base}}{NaOH} + \underset{\text{Acid}}{HCl} \longrightarrow \underset{\text{Salt}}{NaCl} + H_2O$$

- when dissolved in water, these salts dissociate in to ions, this process is called ionisation.
- Salt may be neutral or acidic or basic, its depends on extent on neutrilisation of acid or base
- Mixed salt contains more than one acidic or basic radicals.

example - $NaKSO_4$

② Molecular or addition compounds (आण्विक या योगात्मक यौगिक) :→

- When a solution of two or more simple stable salts are mixed together in simple molecular proportion (सरल आण्विक अनुपात) and the solution thus obtained is allowed to evaporate (वाष्पन), crystals of a new compound are obtained. The new compound is called molecular of addition compound.

example

Simple compounds $\longrightarrow$ Addition compounds

$KCl + MgCl_2 + 6H_2O \longrightarrow KCl \cdot MgCl_2 \cdot 6H_2O$ (carnalite)

$CuSO_4 + 4NH_3 \longrightarrow CuSO_4 \cdot 4NH_3$ (Tetramine copper sulphate)

→ Types of Molecular or addition compounds :→

ⓐ Double salt (द्विक लवण) :→

- These are the addition compounds which are stable in solid state but give their constituent ions (घटक आयन) when dissolved in water or in any other ionic solvent
- In these compounds, the individual properties of constituent ions are not lost.

example :- when Carnalite ($KCl.MgCl_2.6H_2O$) is dissolved in water, its constituent ion namely K^+, Mg^{+2} and Cl^- dissociate in water. i.e. aqueous sol. of carnalite gives the test of K^+, Mg^{+2} and Cl^- ions

Other examples of double salts:→

$$\text{Simple compounds} \longrightarrow \text{Addition compounds}$$

$$K_2SO_4 + Al(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \text{ (potash alum)}$$

$$(NH_4)_2SO_4 + FeSO_4 + 6H_2O \longrightarrow FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \text{ (Mohr's salt)}$$

ⓑ Coordination or complex compound (उपसहसंयोजन या संकुल या जटिल यौगिक) :→

- These are the addition compounds which do not give all their constituent ions when dissolved in water.
- In these compounds, the individual properties of some constitutent ions are lost.

example :- $CuSO_4 \cdot 4NH_3$ does not give test for Cu^{+2} in the aqueous sol., but gives the test for SO_4^{-2} ion and $[Cu(NH_3)_4]^{+2}$ ions.

$$CuSO_4 \cdot 4NH_3 \rightleftharpoons \underset{\text{complex ion}}{[Cu(NH_3)_4]^{+2}} + SO_4^{-2}$$

- In $CuSO_4 \cdot 4NH_3$, individual ions lost their identity.
- Thus $CuSO_4 \cdot 4NH_3$ is formulated as $[Cu(NH_3)_4]SO_4$. this is called coordination or complex compound.

- Types of coordination compounds

(i) compound of simple cation and complex anion

example

$$K_3[Fe(CN)_6] \rightleftharpoons \underset{\text{simple cation}}{3K^+} + \underset{\text{complex anion}}{[Fe(CN)_6]^{-3}}$$

(ii) compound of complex cation and simple anion :-

example

$$[Co(NH_3)_6]Cl_3 \rightleftharpoons \underbrace{[Co(NH_3)_6]^{+3}}_{\text{complex cation}} + \underbrace{3Cl^-}_{\text{simple anion}}$$

(iii) compound of complex cation and complex anion

example

$$[Pt(NH_3)_4][PtCl_4] \rightleftharpoons \underbrace{[Pt(NH_3)_4]^{+2}}_{\text{complex cation}} + \underbrace{[PtCl_4]^{-2}}_{\text{complex anion}}$$

- Neutral complex comp. such as $[Ni(CO_4]^0$, $[Ni(dmg)]^0$ does not give any ion in aq. solution

- coordination comp. are the compounds in which central metal ion is is linked with ligands (+ve ion or -ve ion or neutral molecule) through a donation of lone of e- by ligands to central metal ion.
- coordination comp. may also be defined as the compound which contains complex ions.

Double salt	*Complex compound*
1. It usually contains two simple salts in equimolar proportions.	1. The simple salt from which it formed may or may not be in the equimolar proportions.
2. It exists only in the solid state. In aqueous solution, it dissociates completely into ions.	2. It exists in the solid state as well as in aqueous solution. This is because even in the solution, the complex ion does not dissoiate into ions.
3. It is an ionic compound and does not contain any coordinate bond.	3. It may or may not be ionic but the complex part always contains coordinate bonds.
4. The properties of the double salt are the same as those of its constituents compounds.	4. The properties of the co-ordinate compound are different from its constituents
5. In a double salt, the metal ions show their normal valency.	5. In a coordination compound, the metal ion satisfies its two types of valencies called primary and secondary valencies (discussed later).
6. A double salt loses its identity in the solution.	6. A coordination compound (complex) retains its identity in the solution.

→ **Important Terms used in Coordination compounds :→**

संकुल यौगिकों में प्रयुक्त होने वाले महत्वपूर्ण पद :→

① **coordination chemistry (सहसंयोजन रसायन) :→**

- The branch of chemistry which deals with the study of coordination compounds is known as coordination chemistry.

② **complex Ion (संकुल आयन) :→**

- complex ion is positively or negatively charged species which contains a central metal atom and suitable no. of ligands surrounding the central metal atom.
- The central metal atom may be zero or +ve or -ve oxidation state.
- The ligand may be neutral molecule or anion or cation

example Cationic complex ion →

$[Co(NH_3)_6]^{+3}$, $[Co(NH_3)_5Cl]^{+2}$

Anionic complex ion

$[Ni(CN)_4]^{-2}$, $[Fe(CN)_6]^{-3}$

② Neutral complex (उदासीन संकुल) :→

- A complex which has no charge on it, is called neutral complex.
- It is a non-electrolyte, does not undergo ionisation and hence does not give any ions in aq. solution.

example:- $[Co(NH_3)_3Cl_3]^0$, $[Ni(CO)_4]^0$, $[Fe(CO)_5]^0$, $[Ni(dmg)_2]^0$ etc.

③ Coordination sphere or Coordination entity or Complex entity :→

(सहसंयोजन क्षैत्र था सकुल क्षैत्र या संकुल सत्ता)

- The complex cation or complex anion present in the coordination compound is called coordination sphere.
- The coordination sphere contain central metal atom and ligands. these species enclosed in square bracket [ ].

example In $K_4[Fe(CN)_6]$, $[Fe(CN)_6]^{-4}$ is the coordination sphere.

In $[Cu(NH_3)_4]SO_4$, $[Cu(NH_3)_4]^{+2}$ is the coordination sphere.

④ Central metal atom or Ion (केन्द्रीय धातु परमाणु या आयन) :→

- A metal atom or ion present in a complex ion (coordination entity) is called central metal atom or ion.
- Central metal atom may be +ve, −ve or neutral.
- A fixed no. of ligands are linked with the central metal ion in a fixed geometrical arrangement.
- central metal ion is acts as Lewis acid. because it accepts e⁻ pair from ligands.

example $K_4[Fe(CN)_6]$, Fe is central metal ion

⑤ Ionisation sphere or counter ion (आयनन क्षैत्र या सरल आयन) :→

- The part of complex compound which is present outside the coordination sphere.
- Example $K_4[Fe(CN)_6] \rightarrow K^+$ is counter ion

  $[Cu(NH_3)_4]SO_4 \rightarrow SO_4^{-2}$ is counter ion

⑦ Coordination number of the central metal (केन्द्रीय धातु की समन्वय संख्या) :→

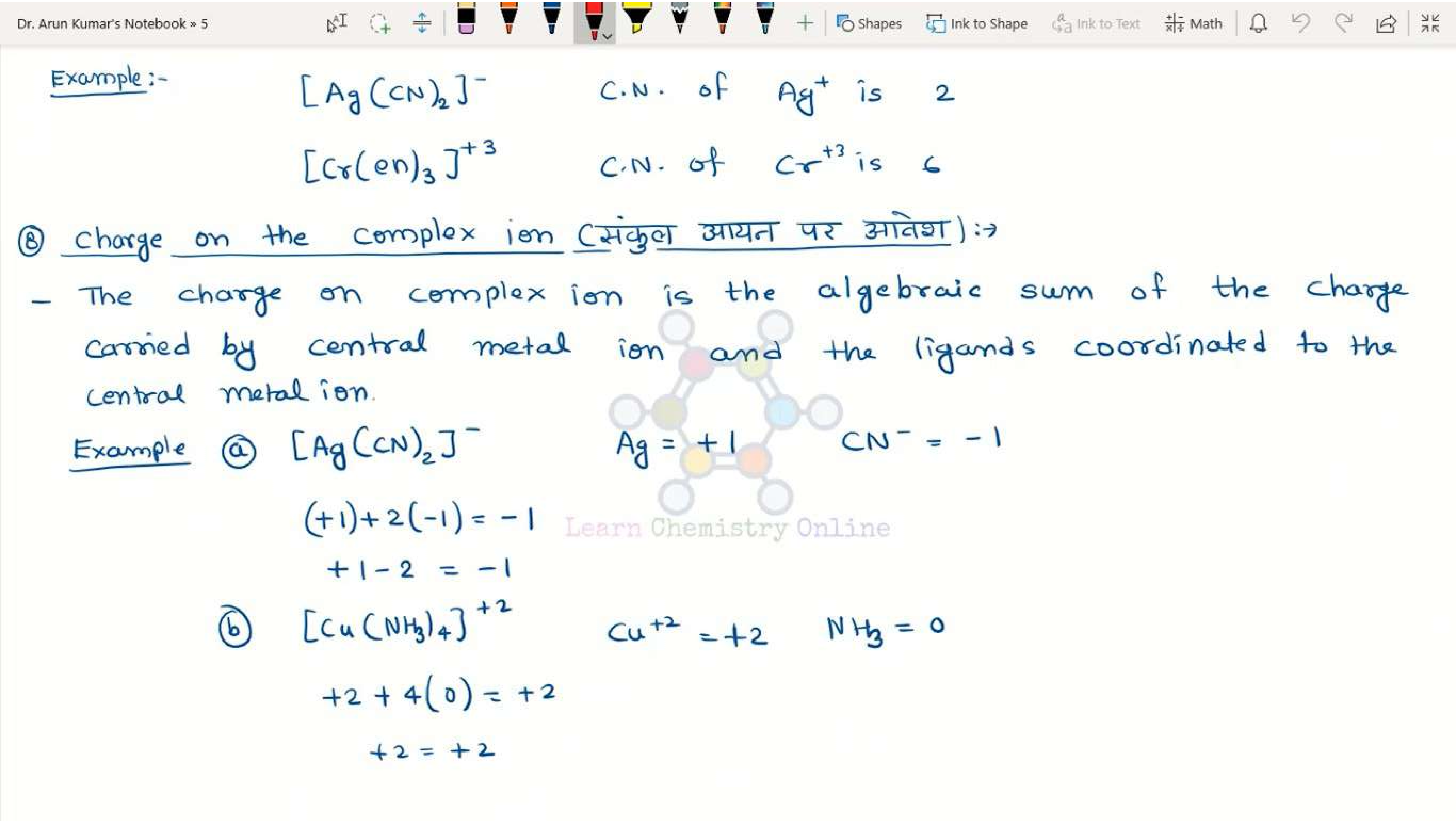
- Coordination no. of central metal/ion is also called ligancy of metal atom/ion.
- Total no. of unidentate or monodentate ligands attached to the central metal ion through coordinate bond or sigma bond is called C.N. of central metal atom/ion.

OR

C.N. of central metal atom/ion may be defined as the number of atoms of the ligands which are attached direcly with the metal atom/ion in coordination sphere.

OR

C.N. is defined as the number of coordinate bonds or sigma bonds formed b/w the central metal atom/ion and donor atom of ligands.



Example :-

$[Ag(CN)_2]^-$ C.N. of Ag^+ is 2

$[Cr(en)_3]^{+3}$ C.N. of Cr^{+3} is 6

⑧ Charge on the complex ion (संकुल आयन पर आवेश) :→

- The charge on complex ion is the algebraic sum of the charge carried by central metal ion and the ligands coordinated to the central metal ion.

Example ⓐ $[Ag(CN)_2]^-$ $Ag = +1$ $CN^- = -1$

$(+1)+2(-1) = -1$

$+1-2 = -1$

ⓑ $[Cu(NH_3)_4]^{+2}$ $Cu^{+2} = +2$ $NH_3 = 0$

$+2+4(0) = +2$

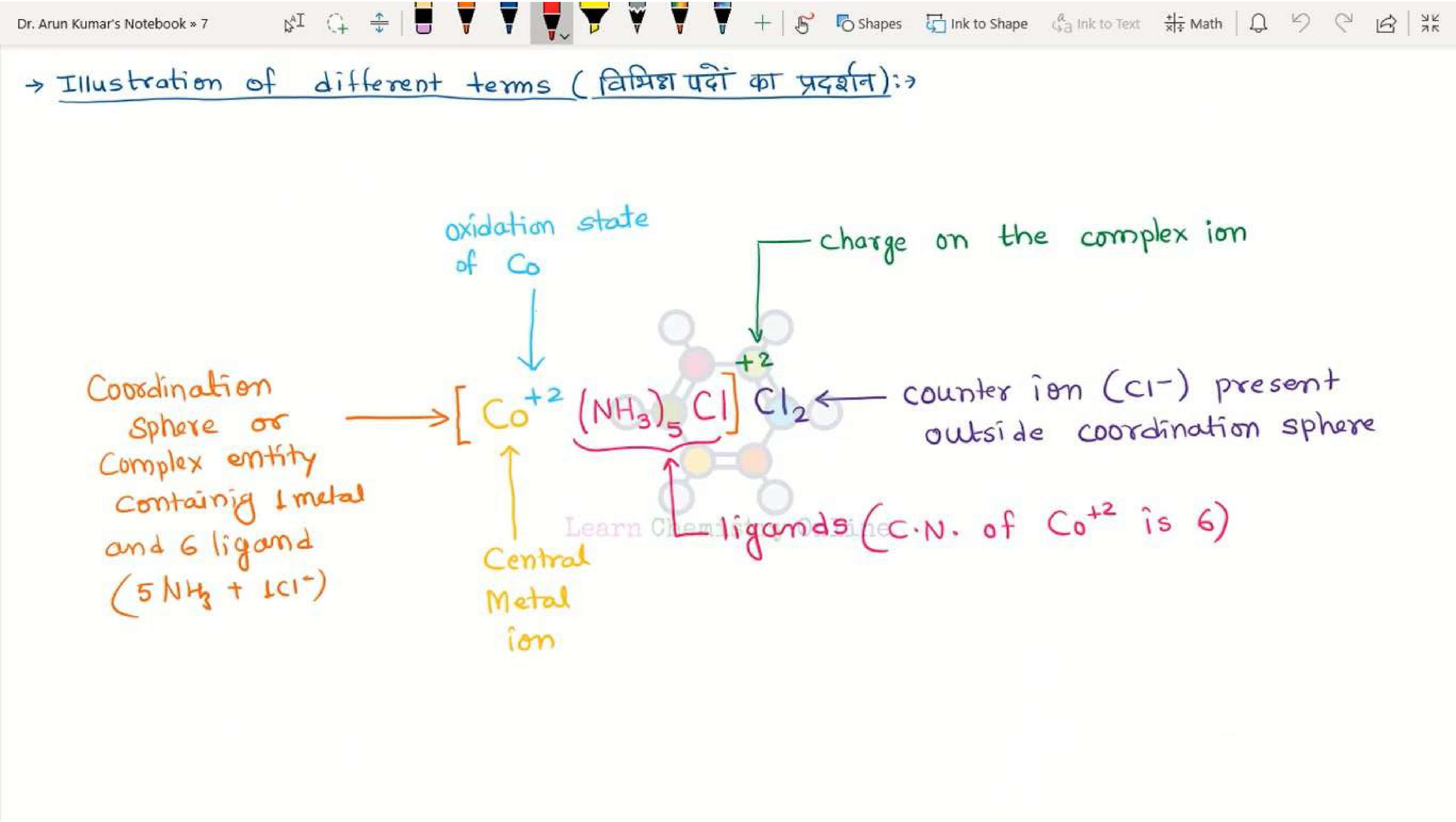
$+2 = +2$

⑨ oxidation number or oxidation state of central metal atom :→

केन्द्रीय धातु परमाणु की ऑक्सीकरण संख्या या ऑक्सीकरण अवस्था :→

- The charge present on central metal atom is called its oxidation state or oxidation number.
- oxidation no. is represented by Roman numerals (I, II, III etc) in paranthesis. (कोष्ठक)
- Calculation:-

ⓐ $[Fe(CN)_6]^{-3}$ ⓑ $[Cu(NH_3)_4]^{+2}$



→ Illustration of different terms (विभिन्न पदों का प्रदर्शन):→

oxidation state of Co

charge on the complex ion

Coordination sphere or Complex entity containig 1 metal and 6 ligand $(5NH_3 + 1Cl^-)$ →

$$[Co^{+2}\underbrace{(NH_3)_5Cl}]^{+2}Cl_2$$

← counter ion (Cl^-) present outside coordination sphere

Central Metal ion

ligands (C.N. of Co^{+2} is 6)

→ Types of complexes (संकुलों के प्रकार) :→

(A) Cationic, Anionic and Neutral complex (धनायनिक, ऋणायनिक तथा उदासीन संकुल) :→

① **Cationic complexes :→**

- A complex in which complex ion carries a net positive charge is called cationic complex.

example :- $[Co(NH_3)_6]^{+3}$, $[Cu(NH_3)_4]^{+2}$ etc.

② **Anionic complexes :→**

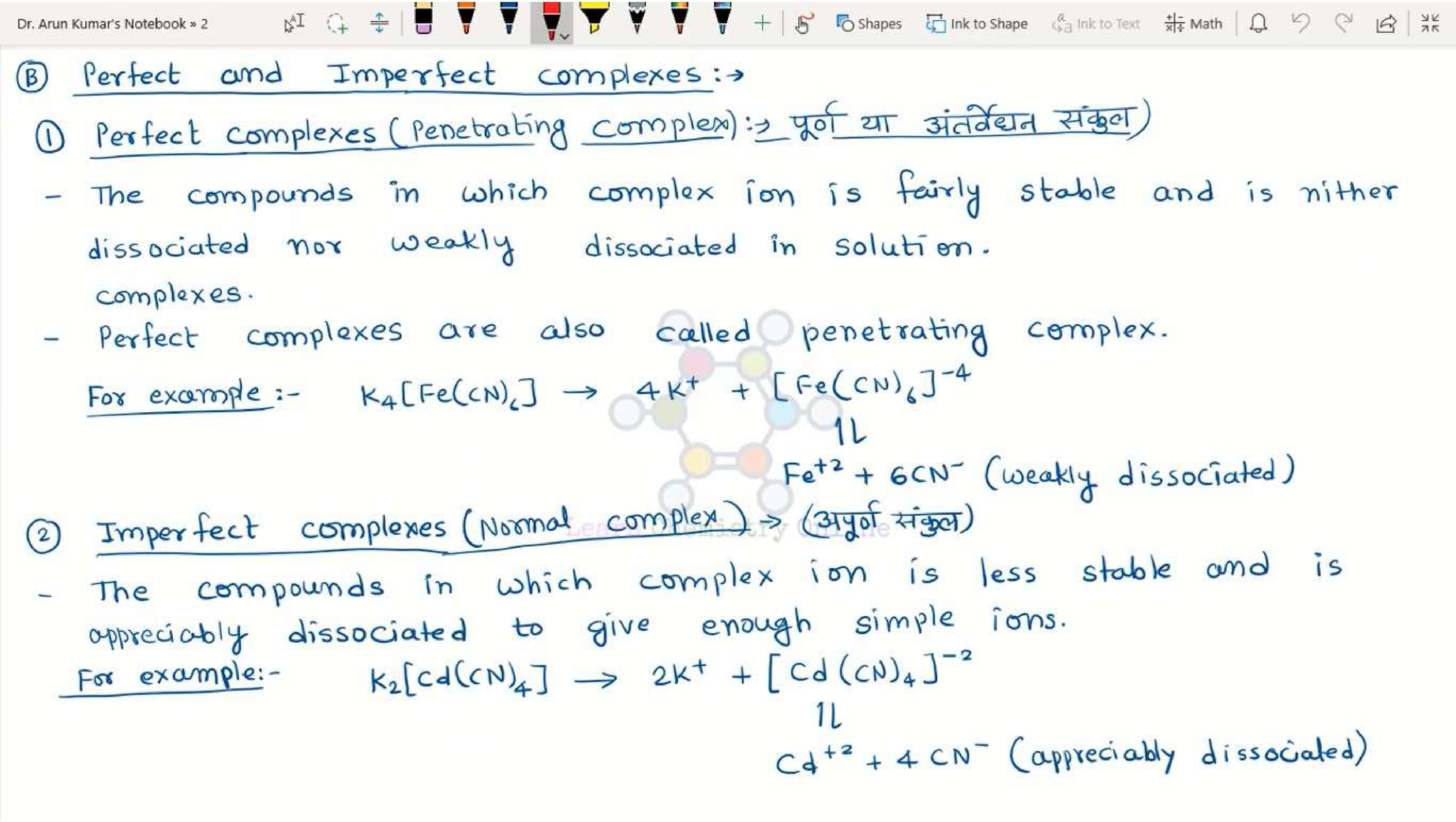
- A complex in which complex ion carries a net negative charge is called anionic complex.

example:- $[Ag(CN)_2]^-$, $[Fe(CN)_6]^{-4}$ etc.

③ **Neutral complexes :→**

- A complex carring no net charge is called a neutral complex or simply a complex

example :- $[Ni(CO)_4]$, $[Co(NH_3)_3Cl_3]$ etc.



Ⓑ Perfect and Imperfect complexes :→

① Perfect complexes (Penetrating complex) :→ पूर्ण या अंतर्वेधन संकुल)

- The compounds in which complex ion is fairly stable and is nither dissociated nor weakly dissociated in solution.

complexes.

- Perfect complexes are also called penetrating complex.

For example :- $K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{-4}$

$$\upharpoonleft\downharpoonright$$

$Fe^{+2} + 6CN^-$ (weakly dissociated)

② Imperfect complexes (Normal complex) → (अपूर्ण संकुल)

- The compounds in which complex ion is less stable and is appreciably dissociated to give enough simple ions.

For example:- $K_2[Cd(CN)_4] \rightarrow 2K^+ + [Cd(CN)_4]^{-2}$

$$\upharpoonleft\downharpoonright$$

$Cd^{+2} + 4CN^-$ (appreciably dissociated)

Ⓒ Labile and Inert complex

① Labile complexes (अस्थिर या चंचल संकुल)

- Those complexes in which ligands can be readily replaced by other ligands (i.e. highly reactive) are called Labile complexes.

② Inert complexes (अक्रिय संकुल)

- Those complexes in which ligands cannot be readily replaced by other ligands (i.e. less reactive) are called Inert complexes.

Ⓓ Homoleptic and Heteroleptic complexes:-

① Homoleptic complexes (होमोलेप्टिक संकुल)

- complexes in which the metal ion/atom is linked with same type of ligand are called Homoleptic complexes. e.g. $[Co(NH_3)_6]^{+3}$

② Heteroleptic complexes (हेट्रोलेप्टिक संकुल)

- Complexes in which the metal ion/atom is linked with different type of ligands are called Heteroleptic complexes. e.g. $[Co(NH_3)_4Cl_2]^+$

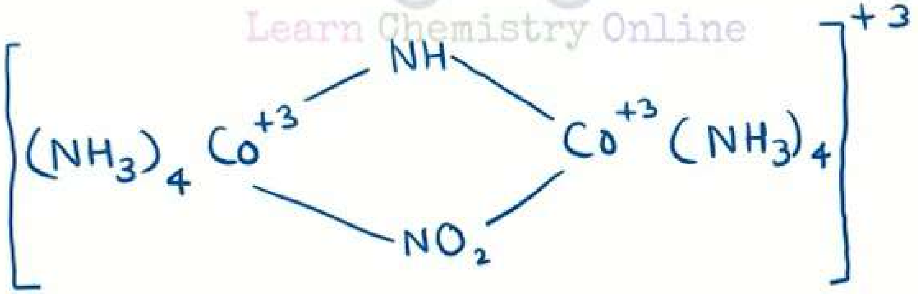
Ⓔ Mononuclear and Polynuclear Complexes :→

① Mononuclear complexes (एककेन्द्रकीय संकुल):→

- These complexes have only one metal atom / ion.
- Example :- $[Co(NH_3)_6]^{+3}$

② Polynuclear complexes (बहुकेन्द्रकीय संकुल):→

- These complexes have two or more than two metal atom/ion.
- Metal atoms or ions are linked together by bridging ligands.
- Example :-

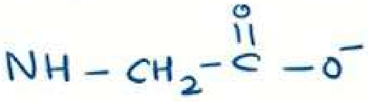


Ⓕ Inner metallic complexes of 1st order and 2nd order :→

① 1st order :→

- The complexes in which the C.N. and charge on the central metal atom are internally fully satisfied at the same time by the coordinate ligands are called inner metallic complex of 1st order.

Example :- $[Co^{+3}(gly)_3]^0$ Gly → Glycinato



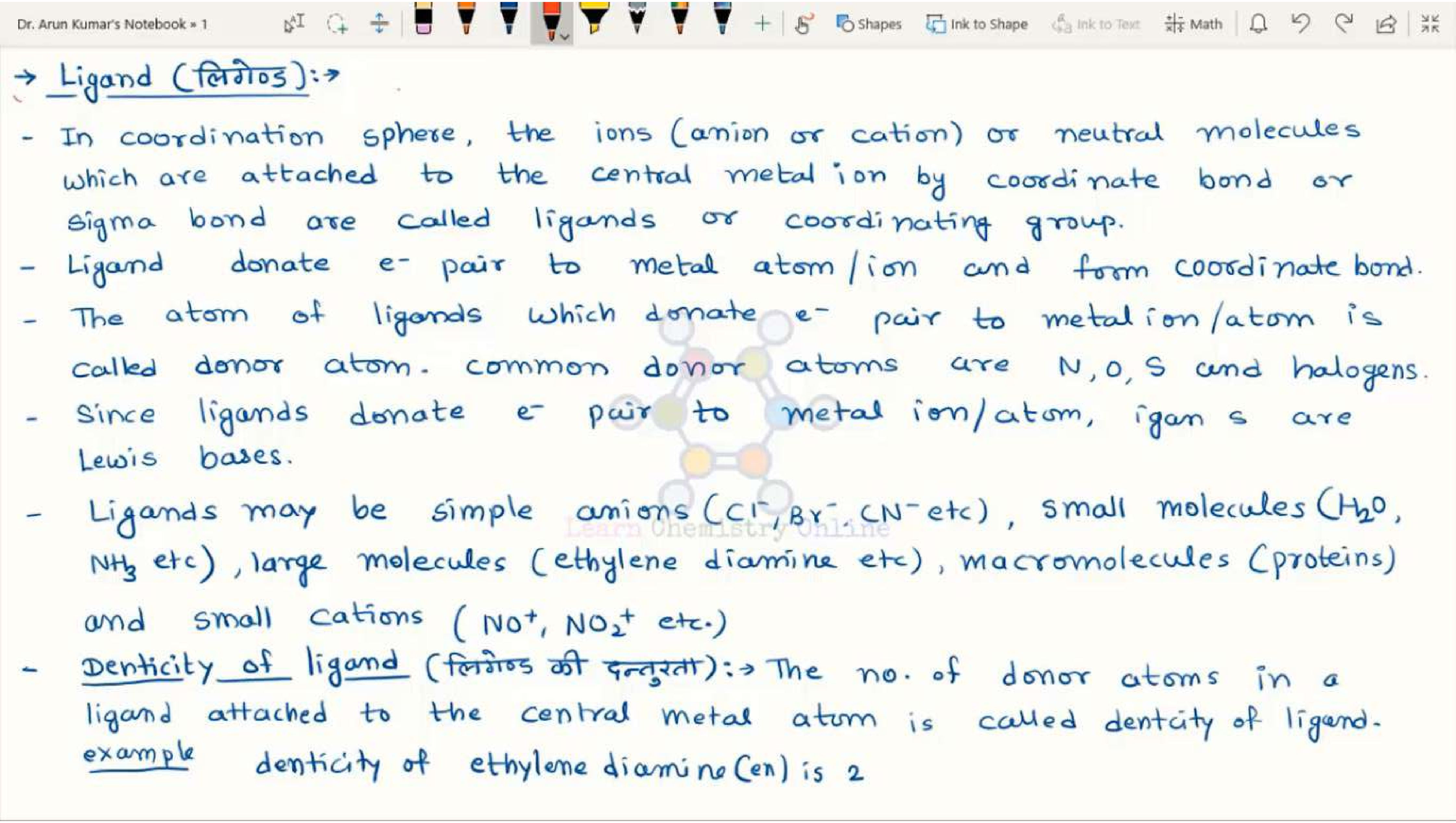
$NH-CH_2-\overset{O}{\overset{||}{C}}-O^-$

② 2nd order :→

- The complexes in which the C.N. and charge of the central metal atom are not fully satisfied at the same time is called inner metallic complex of 2nd order.

- These complexes are ionic species.

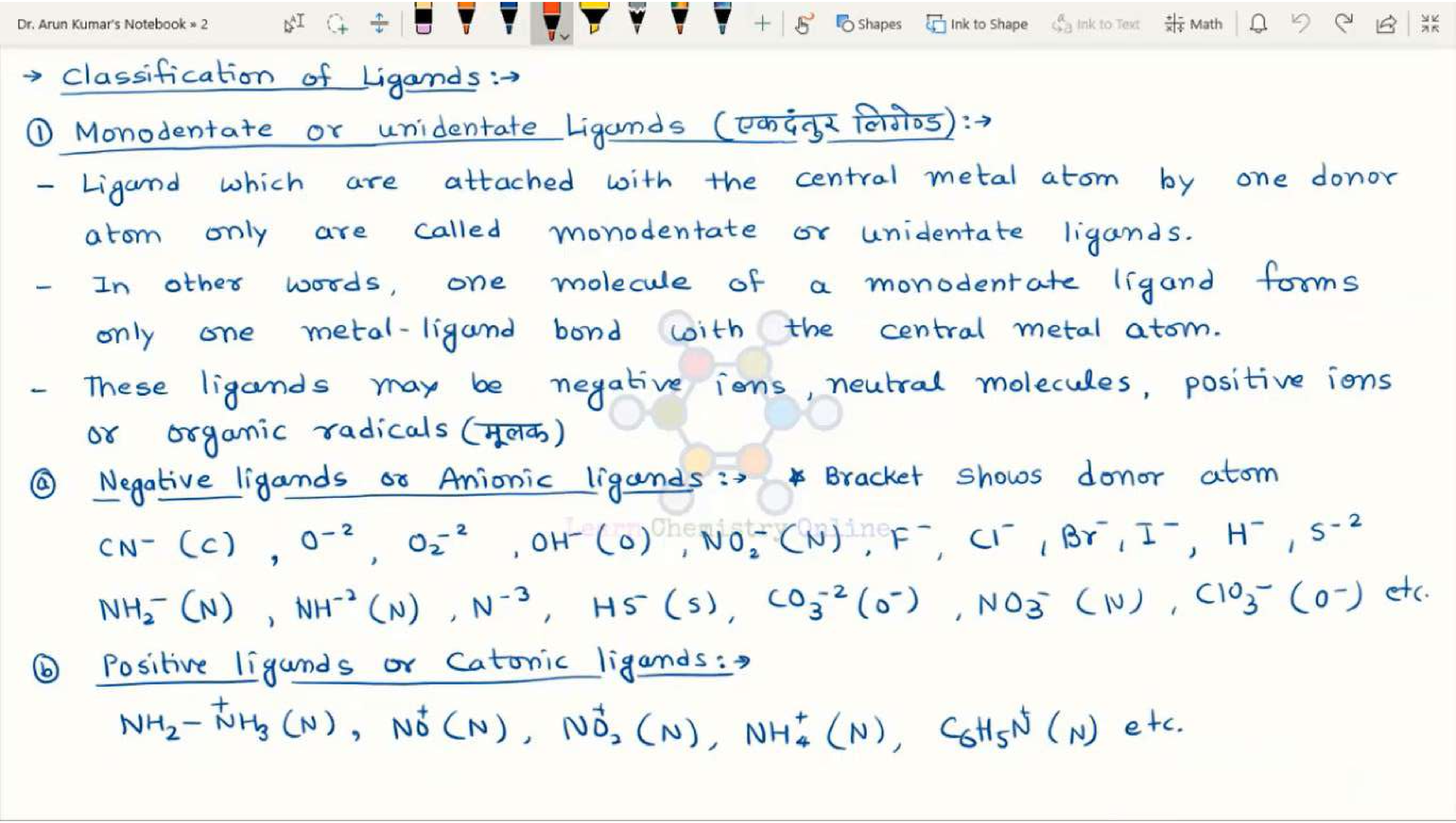
Example $[Fe^{+3}Cl_4]^{-1}$



→ **Ligand (लिगेंड्स):→**

- In coordination sphere, the ions (anion or cation) or neutral molecules which are attached to the central metal ion by coordinate bond or sigma bond are called ligands or coordinating group.
- Ligand donate e- pair to metal atom/ion and form coordinate bond.
- The atom of ligands which donate e- pair to metal ion/atom is called donor atom. common donor atoms are N, O, S and halogens.
- Since ligands donate e- pair to metal ion/atom, igan s are Lewis bases.
- Ligands may be simple anions (Cl^-, Br^-, CN^- etc), small molecules (H_2O, NH_3 etc), large molecules (ethylene diamine etc), macromolecules (proteins) and small cations (NO^+, NO_2^+ etc.)
- **Denticity of ligand** (लिगेंड्स की दन्तुरता):→ The no. of donor atoms in a ligand attached to the central metal atom is called dentcity of ligand.

example denticity of ethylene diamine (en) is 2



→ Classification of Ligands :→

① Monodentate or unidentate Ligands (एकदंतुर लिगेंड्स) :→

- Ligand which are attached with the central metal atom by one donor atom only are called monodentate or unidentate ligands.
- In other words, one molecule of a monodentate ligand forms only one metal-ligand bond with the central metal atom.
- These ligands may be negative ions, neutral molecules, positive ions or organic radicals (मूलक)

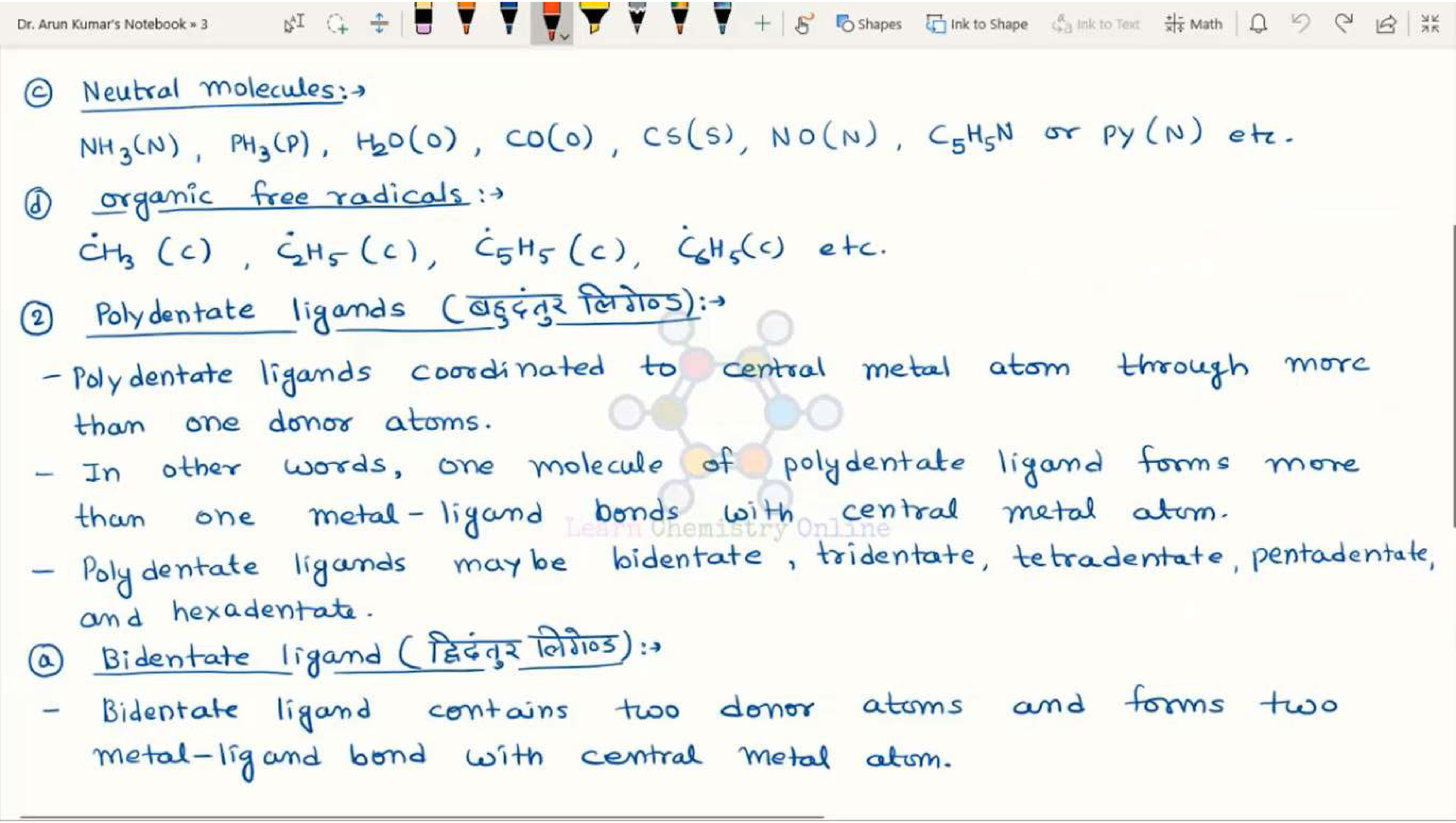
ⓐ Negative ligands or Anionic ligands :→ * Bracket shows donor atom

CN^- (C), O^{-2}, O_2^{-2}, OH^- (O), NO_2^- (N), F^-, Cl^-, Br^-, I^-, H^-, S^{-2}

NH_2^- (N), NH^{-2} (N), N^{-3}, HS^- (S), CO_3^{-2} (O^-), NO_3^- (N), ClO_3^- (O^-) etc.

ⓑ Positive ligands or Cationic ligands :→

$NH_2-\overset{+}{N}H_3$ (N), NO^+ (N), NO_2^+ (N), NH_4^+ (N), $C_6H_5N^+$ (N) etc.



ⓒ **Neutral molecules:→**

$NH_3(N)$, $PH_3(P)$, $H_2O(O)$, $CO(O)$, $CS(S)$, $NO(N)$, C_5H_5N or py (N) etc.

ⓓ **organic free radicals:→**

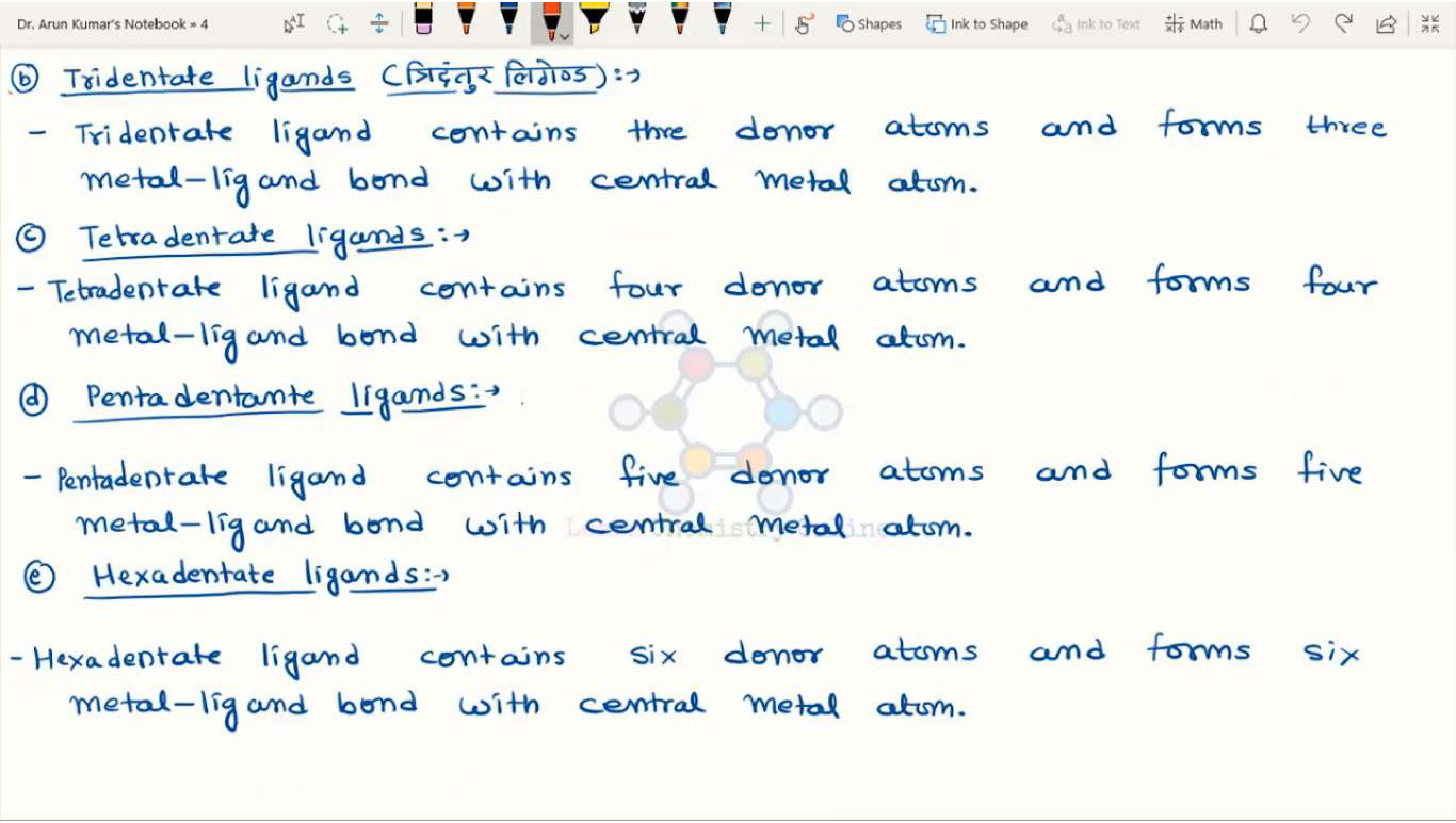
$\dot{C}H_3$ (c), $\dot{C}_2H_5$ (c), $\dot{C}_5H_5$ (c), $\dot{C}_6H_5$ (c) etc.

② **Polydentate ligands (बहुदंतुर लिगेण्ड्स):→**

- Polydentate ligands coordinated to central metal atom through more than one donor atoms.
- In other words, one molecule of polydentate ligand forms more than one metal-ligand bonds with central metal atom.
- Polydentate ligands may be bidentate, tridentate, tetradentate, pentadentate, and hexadentate.

ⓐ **Bidentate ligand (द्विदंतुर लिगेण्ड्स):→**

- Bidentate ligand contains two donor atoms and forms two metal-ligand bond with central metal atom.



ⓑ Tridentate ligands (त्रिदंतुर लिगेंड्स):→

- Tridentate ligand contains thre donor atoms and forms three metal-ligand bond with central metal atom.

ⓒ Tetradentate ligands:→

- Tetradentate ligand contains four donor atoms and forms four metal-ligand bond with central metal atom.

ⓓ Pentadentante ligands:→

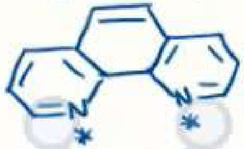
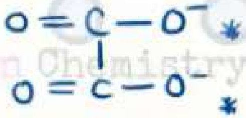
- Pentadentate ligand contains five donor atoms and forms five metal-ligand bond with central metal atom.

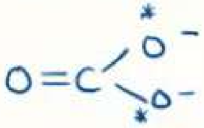
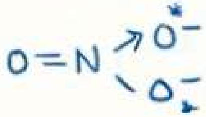
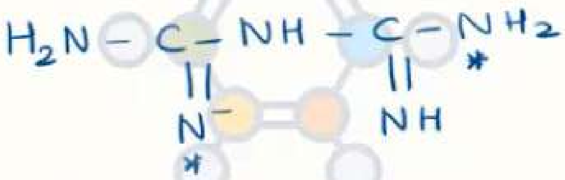
ⓔ Hexadentate ligands:→

- Hexadentate ligand contains six donor atoms and forms six metal-ligand bond with central metal atom.

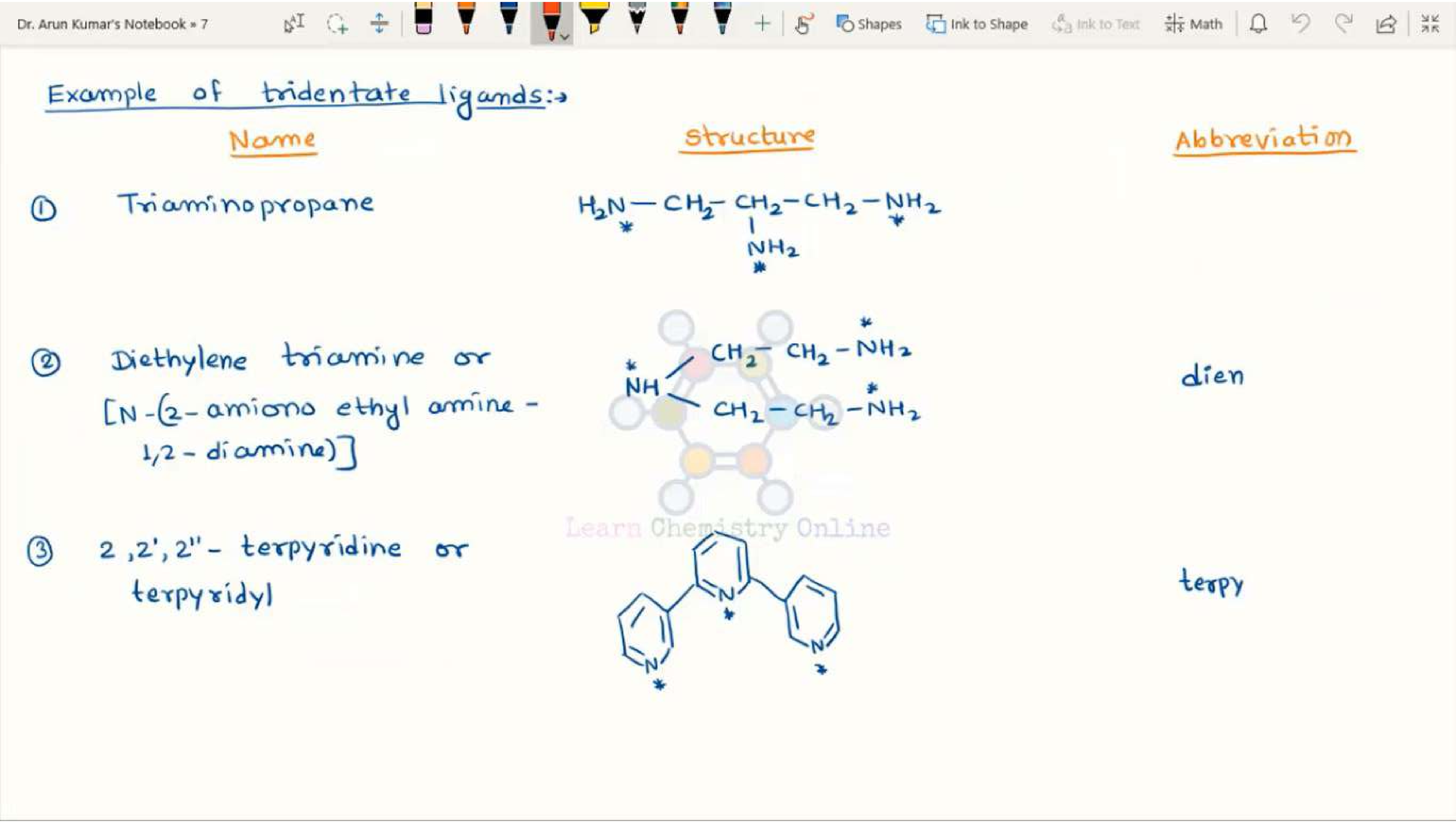
- Examples of bidentate ligands :→

* → Represents donor atoms

Name	Structure	Abbreviation
① 2,2,2- bipyridine		bipy or bipyridyl
② o - phenanthroline or 1,10 - phenanthroline		o-phen or phen or phenan
③ Acetylacetonato ion	 $CH_3-\underset{\underset{O^{*}}{\|}}{C}-CH=\underset{\underset{O^{-*}}{\vert}}{C}-CH_3$	$acac^-$
④ Oxalato ion ($C_2O_4^{-2}$)	 $\begin{array}{l} O=C-O^{-*} \\ \quad\ \vert \\ O=C-O^{-*} \end{array}$	ox^{-2}
⑤ Dimethylglyoximato ion	 $\begin{array}{l} CH_3-C=\overset{*}{N}-OH \\ \qquad\ \vert \\ CH_3-C=\overset{*}{N}-O^- \end{array}$	dmg^- or DMG^-
⑥ Glycinato ion	 $H_2\underset{*}{N}-CH_2-\underset{\underset{O}{\|}}{C}-O^-_{*}$	gly^-

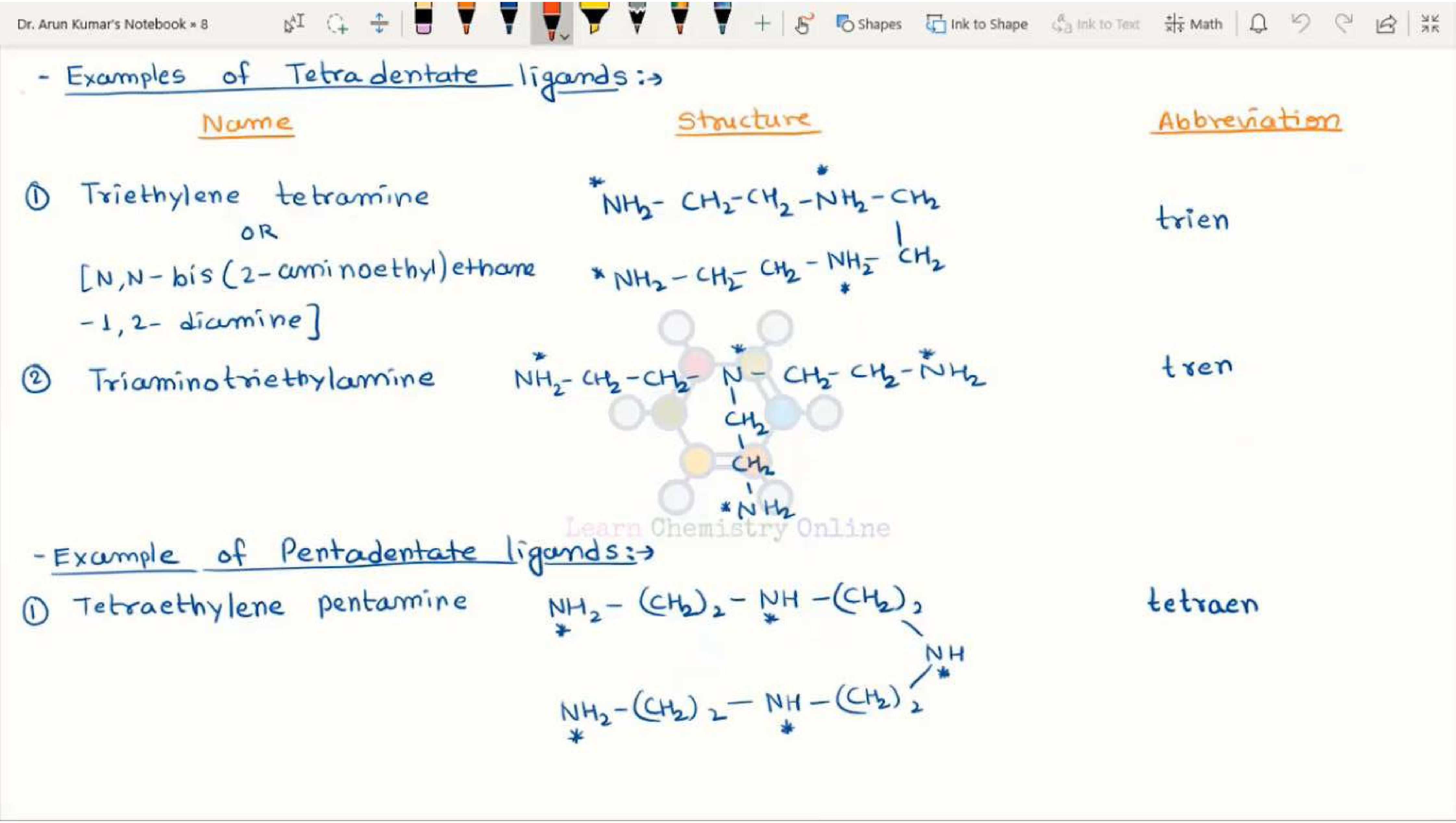
	Name	Structure	Abbreviation
⑦	Carbonato (CO_3^{-2})		
⑧	Nitrato (NO_3^-)		
⑨	Sulphato (SO_4^{-2})		
⑩	Biguanido ion		big$^-$
⑪	Ethylene diamine or ethane-1,2-diamine	$H_2\overset{*}{N}-CH_2-CH_2-\overset{*}{N}H_2$	en

* These three ligands also acts as monodentate ligands



Example of tridentate ligands:→

Name	Structure	Abbreviation
① Triaminopropane	$\underset{*}{H_2N}-CH_2-\underset{\underset{*}{NH_2}}{\underset{\vert}{CH_2}}-CH_2-\underset{*}{NH_2}$	
② Diethylene triamine or [N-(2-amiono ethyl amine - 1,2 - diamine)]	$\overset{*}{NH}\begin{array}{l}CH_2-CH_2-\overset{*}{NH_2}\\CH_2-CH_2-\overset{*}{NH_2}\end{array}$	dien
③ 2,2',2''- terpyridine or terpyridyl		terpy

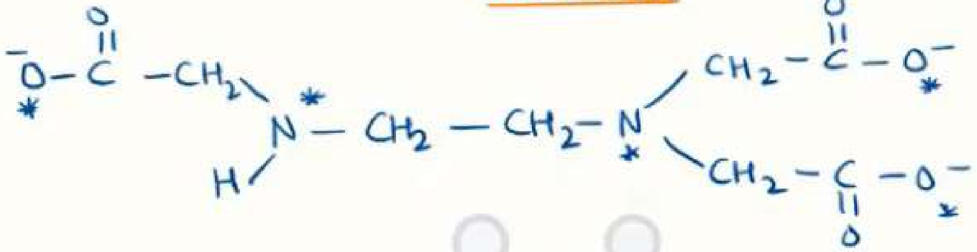


- Examples of Tetradentate ligands :→

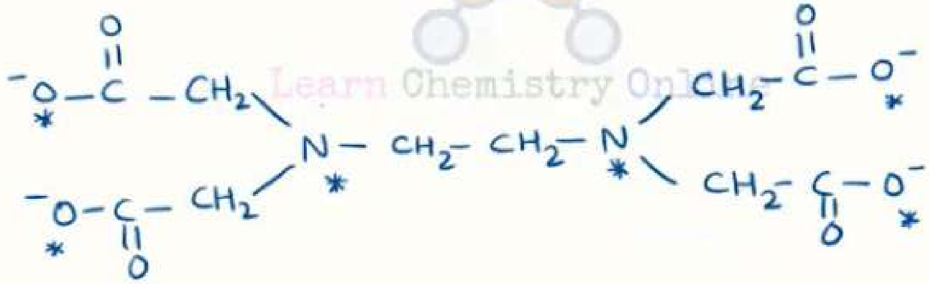
Name	Structure	Abbreviation
① Triethylene tetramine OR [N,N-bis(2-aminoethyl)ethane -1,2- diamine]	$^{*}NH_2-CH_2-CH_2-\overset{*}{N}H_2-CH_2$ $\vert$ $^{*}NH_2-CH_2-CH_2-\underset{*}{N}H_2-CH_2$	trien
② Triaminotriethylamine	$\overset{*}{N}H_2-CH_2-CH_2-\overset{*}{N}-CH_2-CH_2-\overset{*}{N}H_2$ $\vert$ CH_2 $\vert$ CH_2 $\vert$ $^{*}NH_2$	tren

- Example of Pentadentate ligands:→

① Tetraethylene pentamine	$\underset{*}{N}H_2-(CH_2)_2-\underset{*}{N}H-(CH_2)_2$ $\backslash$ $\underset{*}{N}H$ $/$ $\underset{*}{N}H_2-(CH_2)_2-\underset{*}{N}H-(CH_2)_2$	tetraen

Name	Structure	Abbreviation
② Ethylene diamine triacetato ion		$edta^{-3}$

Example of Hexadentate ligand :→

① Ethylene diamine tetracetato ion		$edta^{-4}$

③ **π- Acid ligands (π- acceptors):→**

- The ligand which can accept e⁻ density from the filled d-orbitals of the metal ion into their Vacant π or π* orbitals are called π-acid ligands or π acceptors. example - CO (carbonyl ligand)

④ **Ambidentate ligand (उभयदन्तुक लिगेण्ड्स):→**

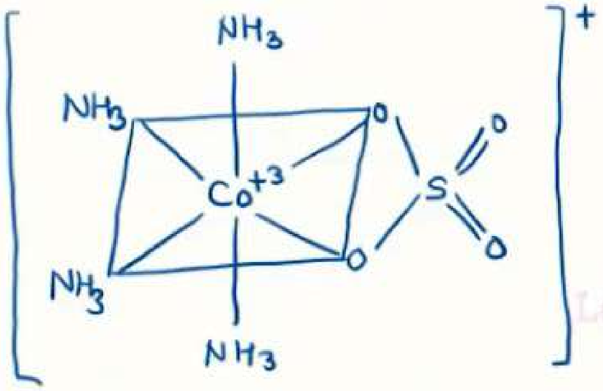
- There are some ligands which have two or more donor atoms but in forming complexes only one donor atom is attached to the metal ion at a given time. such ligands are called ambidentate ligands.

- example
  ① ${}^{*}\ddot{\bar{C}}\equiv N:$ cyno ligand $:\overset{-}{\underset{*}{N}}=C:$ Isocyano ligand
  ② $:\ddot{O}\leftarrow\overset{..}{\underset{*}{N}}=\ddot{O}:$ Nitro ligand $:\overset{-}{\underset{*}{O}}-\ddot{N}=\ddot{O}:$ Nitrito ligand
  ③ ${}^{*}\bar{O}CN$ cyanato ligand ${}^{*}\bar{N}CO$ Isocyanoto ligand
  ④ ${}^{*}\bar{S}CN$ Thiocyanato ligand ${}^{*}\bar{N}CS$ Isothiocyanato ligand

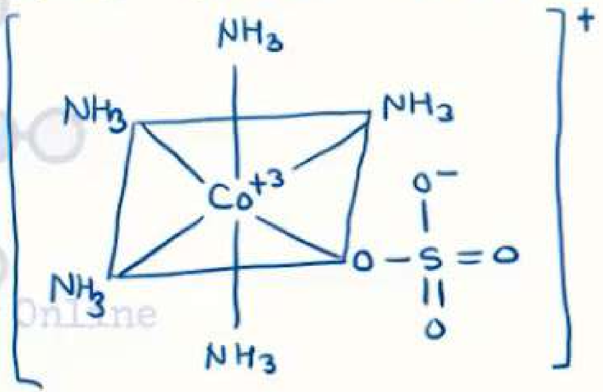
⑤ Flexidentate ligand

- sometimes polydentate ligands do not use all their donor atoms to form coordinate bonds with the central metal atom or ion. This character of polydentate ligand is called their flexidentate character and the ligands are called flexidentate ligand.

example SO_4^{-2}, CO_3^{-2}, N_2, OH^-, NH_2^-, Cl^-, O_2^{-2}, $EDTA^{-4}$ ion etc.



$[Co(NH_3)_4(SO_4)]^+$



$[Co(NH_3)_5(SO_4)]^+$

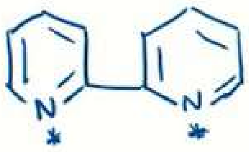
⑥ Bridging Ligands (सेतु लिगेण्ड):→

- Monodentate ligand having more than one free e^- pair, forms two σ bonds with two metal atoms and thus acts as bridge between the metal atoms. Such a ligand is called bridging ligand and complex is called bridged complex
- Example – OH^-, F^-, Cl^-, NH_2^-, CO, O^{-2}, SO_4^{-2} etc. $[(NH_3)_5Cr{-}OH{-}Cr(NH_3)_5]Cl_5$

⑦ Symmetrical and unsymmetrical bidentate ligands:→

- In symmetrical bidentate ligand, the two coordinating or donor atoms are same

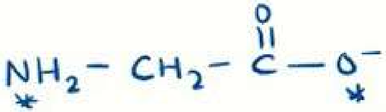
Example:-



Dipyridyl

- In unsymmetrical bidentate ligand, the two coordinating or donor atoms are different.

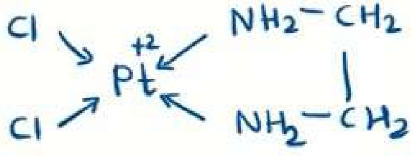
Example:-



$\overset{*}{N}H_2-CH_2-\overset{O}{\overset{\|}{C}}-\overset{*}{O^-}$ Glycinato

→ Chelates, chelating ligand and chelation :→
कीलेट, कीलेट लिगेंड्स तथा कीलेटीकरण :→

- Chelate → from Greek word "claw" (पंजा)
- When a polydentate or multidentate ligand simultaneously coordinates to a metal ion through more than one sigma e⁻ pair donor site or atom, a ring like structure is formed. It is called chelate and the ligand is called chelating ligand. The process of formation of rings is called chelation.
- The term chelation is also called cyclisation (चक्रीकरण).
- chelat is also known as metal chelates, chelated complexes. etc.
- **Example** – Ethylene diamine as chelating ligand ($\overset{*}{N}H_2-CH_2-CH_2-\overset{*}{N}H_2$)



Structure of $[Pt^{+2}Cl_2(en)]^0$

✱ Every multidentate or polydentate ligand is not necessarily a chelating ligand.

→ Chelate effect (कीलेट प्रभाव):→

- chelated complexes (containing 5 or 6 membered ring including metal atom) are more stable than the non-chelated complexes. Greater stability of chelated complexes is called chelate effect.
- Stability of complex ∝ No. of ring present in complex

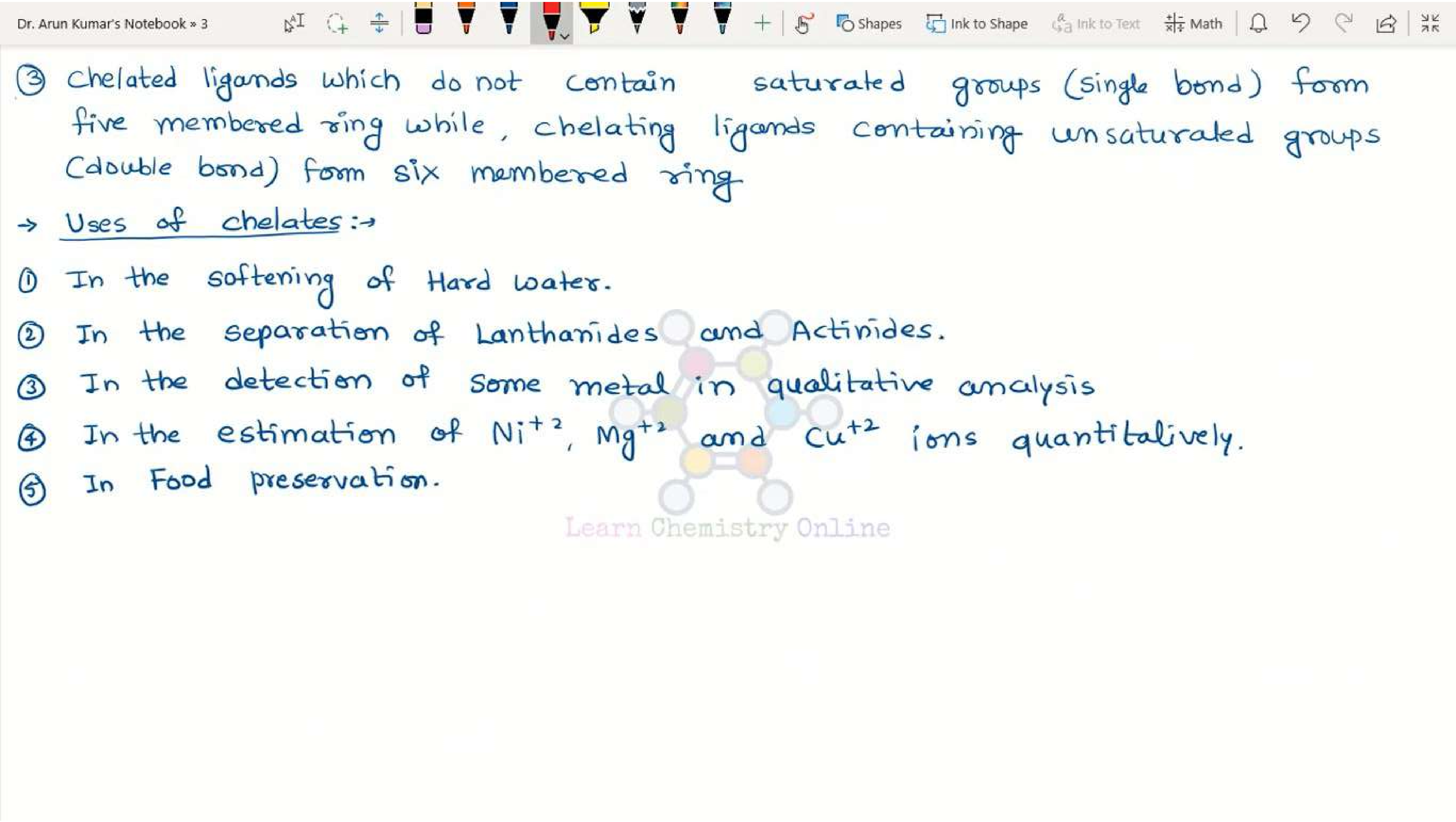
Example

$[Cu(en)_2]^{2+}$	$[Fe(edta)]^-$
- two rings	- five rings
- less stable	- more stable

→ Characteristics of chelates:→

① chelate are more stable than complex containing monodentate ligands. This is because when chelation occurs, entropy of the system increases and the process is more favourable

② Ligands with large groups form unstable rings than the ligands with smaller groups due to steric hinderance (त्रिविम बाधा).



③ Chelated ligands which do not contain saturated groups (single bond) form five membered ring while, chelating ligands containing unsaturated groups (double bond) form six membered ring

→ Uses of chelates :→

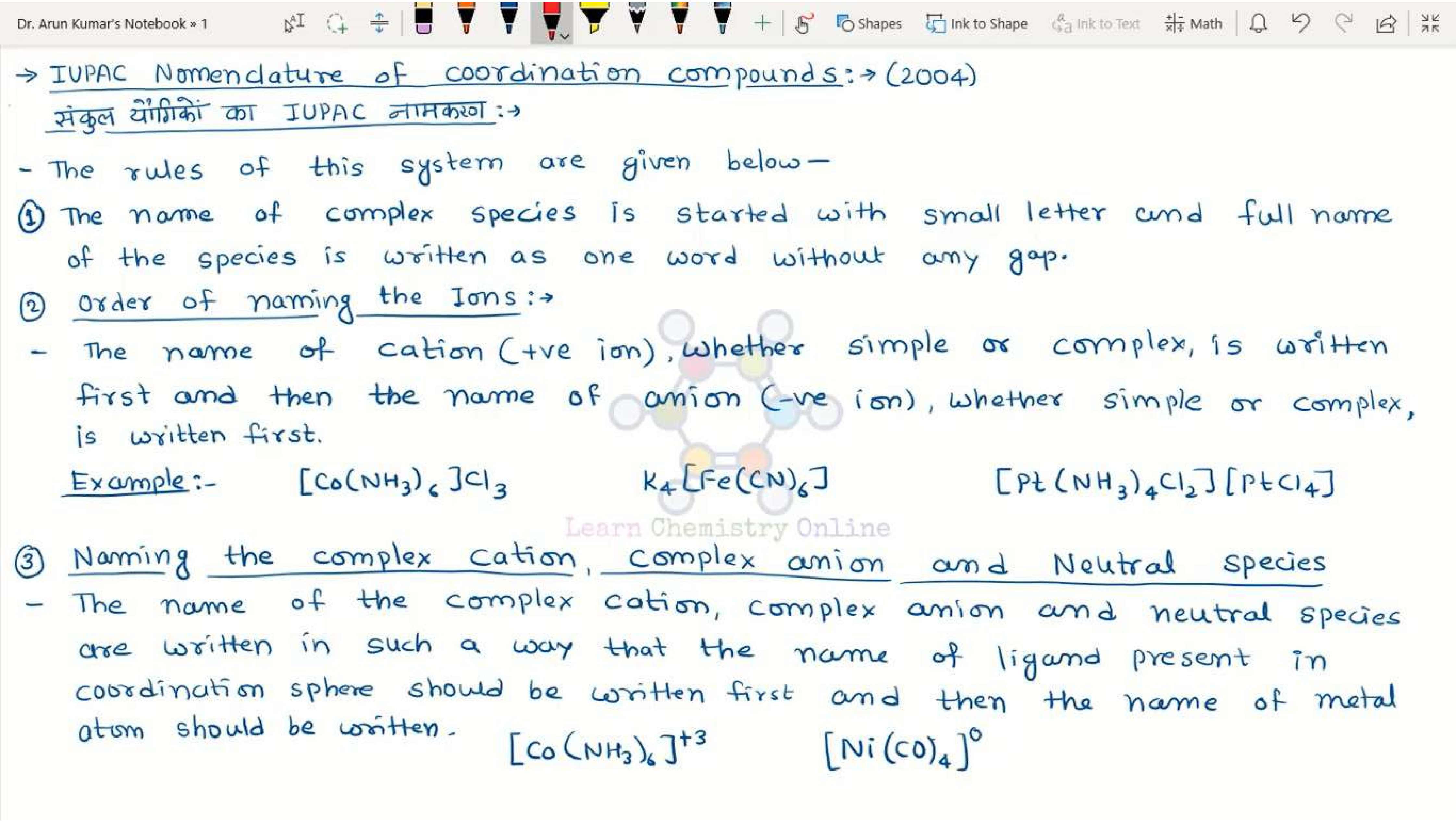
① In the softening of Hard water.

② In the separation of Lanthanides and Actinides.

③ In the detection of some metal in qualitative analysis

④ In the estimation of Ni^{+2}, Mg^{+2} and Cu^{+2} ions quantitatively.

⑤ In Food preservation.



→ IUPAC Nomenclature of coordination compounds :→ (2004)

संकुल यौगिकों का IUPAC नामकरण :→

- The rules of this system are given below –

① The name of complex species is started with small letter and full name of the species is written as one word without any gap.

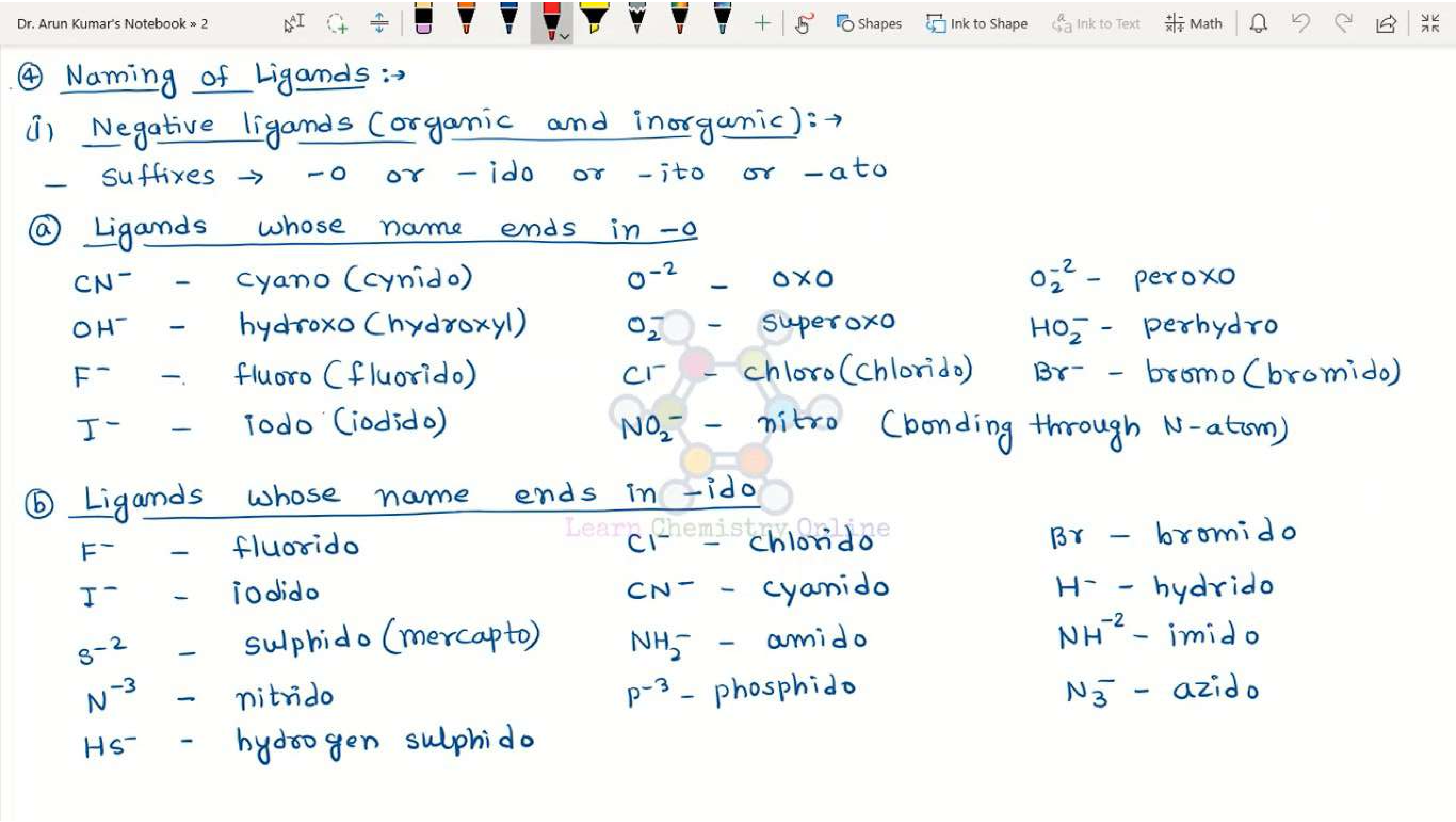
② Order of naming the Ions :→

- The name of cation (+ve ion), whether simple or complex, is written first and then the name of anion (-ve ion), whether simple or complex, is written first.

Example :- $[Co(NH_3)_6]Cl_3$ $K_4[Fe(CN)_6]$ $[Pt(NH_3)_4Cl_2][PtCl_4]$

③ Naming the complex cation, complex anion and Neutral species

- The name of the complex cation, complex anion and neutral species are written in such a way that the name of ligand present in coordination sphere should be written first and then the name of metal atom should be written. $[Co(NH_3)_6]^{+3}$ $[Ni(CO)_4]^0$



④ Naming of Ligands :→

(i) Negative ligands (organic and inorganic):→

- suffixes → -o or -ido or -ito or -ato

ⓐ Ligands whose name ends in -o

CN^- - cyano (cynido)
OH^- - hydroxo (hydroxyl)
F^- - fluoro (fluorido)
I^- - iodo (iodido)

O^{-2} - oxo
O_2^- - superoxo
Cl^- - chloro (chlorido)
NO_2^- - nitro (bonding through N-atom)

O_2^{-2} - peroxo
HO_2^- - perhydro
Br^- - bromo (bromido)

ⓑ Ligands whose name ends in -ido

F^- - fluorido
I^- - iodido
S^{-2} - sulphido (mercapto)
N^{-3} - nitrido
HS^- - hydrogen sulphido

Cl^- - chlorido
CN^- - cyanido
NH_2^- - amido
P^{-3} - phosphido

Br - bromido
H^- - hydrido
NH^{-2} - imido
N_3^- - azido

ⓒ Ligands whose names end in -ito

SO_3^{-2} - sulphito

ONO^- - nitrito (bonding through O-atom)

ⓓ Ligands whose names end in -ato

CO_3^{-2} - carbonato

SO_4^{-2} - sulphato

NO_3^- - nitrato

$S_2O_3^{-2}$ - thiosulphato

CH_3COO^- - acetato

ClO_3^- - chlorato

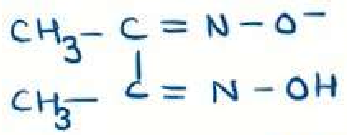
SCN^- - thiocyanato

NCS^- - isothiocyanato (bonding through N-atom)

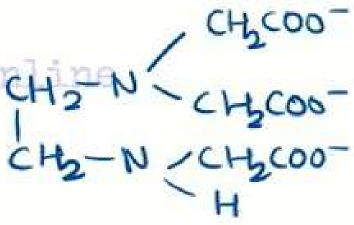
$C_2O_4^{-2}$ - oxalato (ox^{-2})

$H_2N-CH_2-COO^-$ - Glycinato (gly^-)

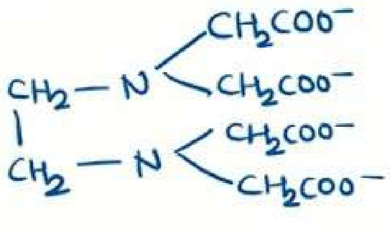
$CH_3-\underset{\underset{O}{\|}}{C}-CH-\underset{\underset{O^-}{|}}{C}-CH_3$ - Acetylacetonato ($acac^-$)



- Dimetylglyoxamato (dmg^-)



Ethylenediamine triacetato ion ($edta^{-3}$)



Ethylenediamine tetraacetato ($edta^{-4}$)

(ii) Neutral ligands :→

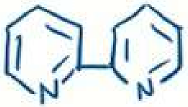
— No special suffix

NH_3 - amine H_2O - aqua CO - Carbonyl CS - thiocarbonyl

N_2 - nitrosyl O_2 - (dioxygen) N_2 - (dinitrogen) CH_3NH_2 - methyl amine

PH_3 - phosphine $(C_6H_5)_P$ - triphenylphosphine $H_2N\text{-}CS\text{-}NH_2$ - thiourea (tu)

 or C_5H_5N - pyridine (py)

 — 2,2-dipyridyl (dipy)

$NH_2-(CH_2)_2-NH_2$ - ethylenediamine (en)

$NH_2-(CH_2)_2-NH-(CH_2)_2-NH_2$ — diethylene triamine (dien)

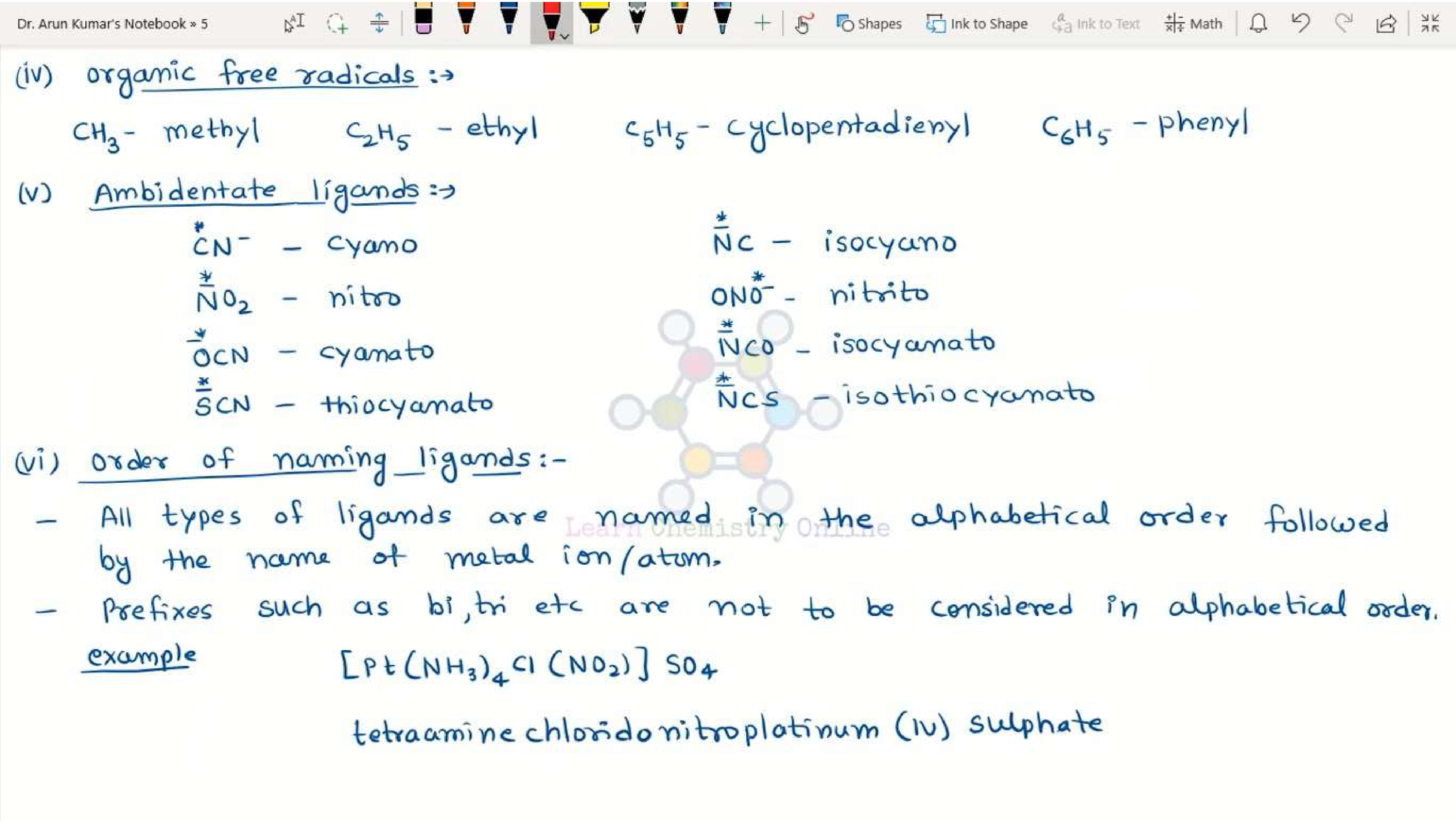
$NH_2-(CH_2)_2-NH-(CH_2)_2-NH-(CH_2)_2-NH_2$ - triethylene tetramine (trien)

 — phenanthroline

(iii) Positive ligands :→ suffix - ium

$NH_2-\overset{+}{N}H_3$ - hydrazinium NO^+ - nitrosonium NO_2^+ - nitronium NH_4^+ - ammonium

$C_5H_5\overset{+}{N}H$ - pyridnium $(C_6H_5)_4P^+$ - tetraphenylphosphonium PH_4^+ - phosphonium



(iv) organic free radicals :→

CH_3- methyl C_2H_5 - ethyl C_5H_5 - cyclopentadienyl C_6H_5 - phenyl

(v) Ambidentate ligands :→

$\overset{*}{C}N^-$ - cyano

$\overset{*}{N}O_2$ - nitro

$\overset{*}{O}CN$ - cyanato

$\overset{*}{S}CN$ - thiocyanato

$\overset{*}{N}C$ - isocyano

$ON\overset{*}{O}^-$ - nitrito

$\overset{*}{N}CO$ - isocyanato

$\overset{*}{N}CS$ - isothiocyanato

(vi) Order of naming ligands :-

- All types of ligands are named in the alphabetical order followed by the name of metal ion/atom.
- Prefixes such as bi, tri etc are not to be considered in alphabetical order.

example $[Pt(NH_3)_4Cl(NO_2)]SO_4$

tetraamine chloridonitroplatinum (IV) sulphate

(vii) Use of numerical prefixes to indicate the no. of ligands:→

ⓐ If the coordination sphere has same type of ligands then the prefixes di, tri, tetra, penta, hexa etc are used

example

$[Cu(NH_3)_4]SO_4$

tetraammine copper (II) sulphate

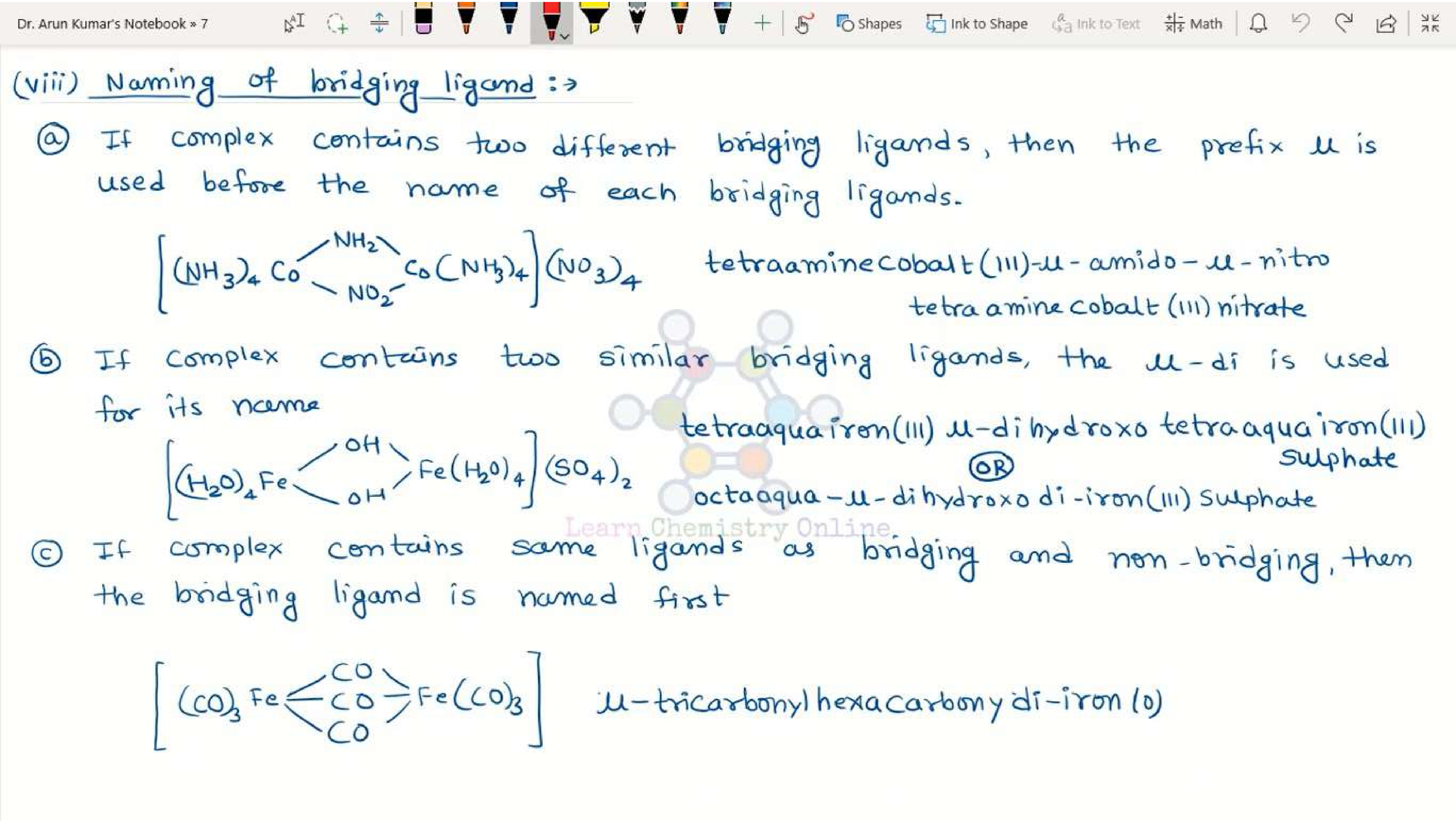
ⓑ If the ligand already contain prefixes such as bi, tri, tetra etc in their names, then following prefixes are used

for two – bis
for three – tris
for four – tetrakis
for five – pentakis
for six – hexakis

- In such case, the name of ligand is written in bracket. ( )

example $[CoCl_2(en)_2]SO_4$

dichlorobis (diemethylamine) cobalt (IV) suphate



(viii) Naming of bridging ligand :→

ⓐ If complex contains two different bridging ligands, then the prefix μ is used before the name of each bridging ligands.

$$\left[(NH_3)_4Co\begin{matrix}\diagup NH_2 \diagdown \\ \diagdown NO_2^- \diagup\end{matrix}Co(NH_3)_4\right](NO_3)_4$$

tetraaminecobalt(III)-μ-amido-μ-nitro tetraaminecobalt(III) nitrate

ⓑ If complex contains two similar bridging ligands, the μ-di is used for its name

$$\left[(H_2O)_4Fe\begin{matrix}\diagup OH \diagdown \\ \diagdown OH \diagup\end{matrix}Fe(H_2O)_4\right](SO_4)_2$$

tetraaquairon(III) μ-dihydroxo tetraaquairon(III) sulphate

OR

octaaqua-μ-dihydroxo di-iron(III) sulphate

ⓒ If complex contains same ligands as bridging and non-bridging, then the bridging ligand is named first

$$\left[(CO)_3Fe\begin{matrix}\diagup CO \diagdown \\ - CO - \\ \diagdown CO \diagup\end{matrix}Fe(CO)_3\right]$$

μ-tricarbonyl hexacarbony di-iron (0)

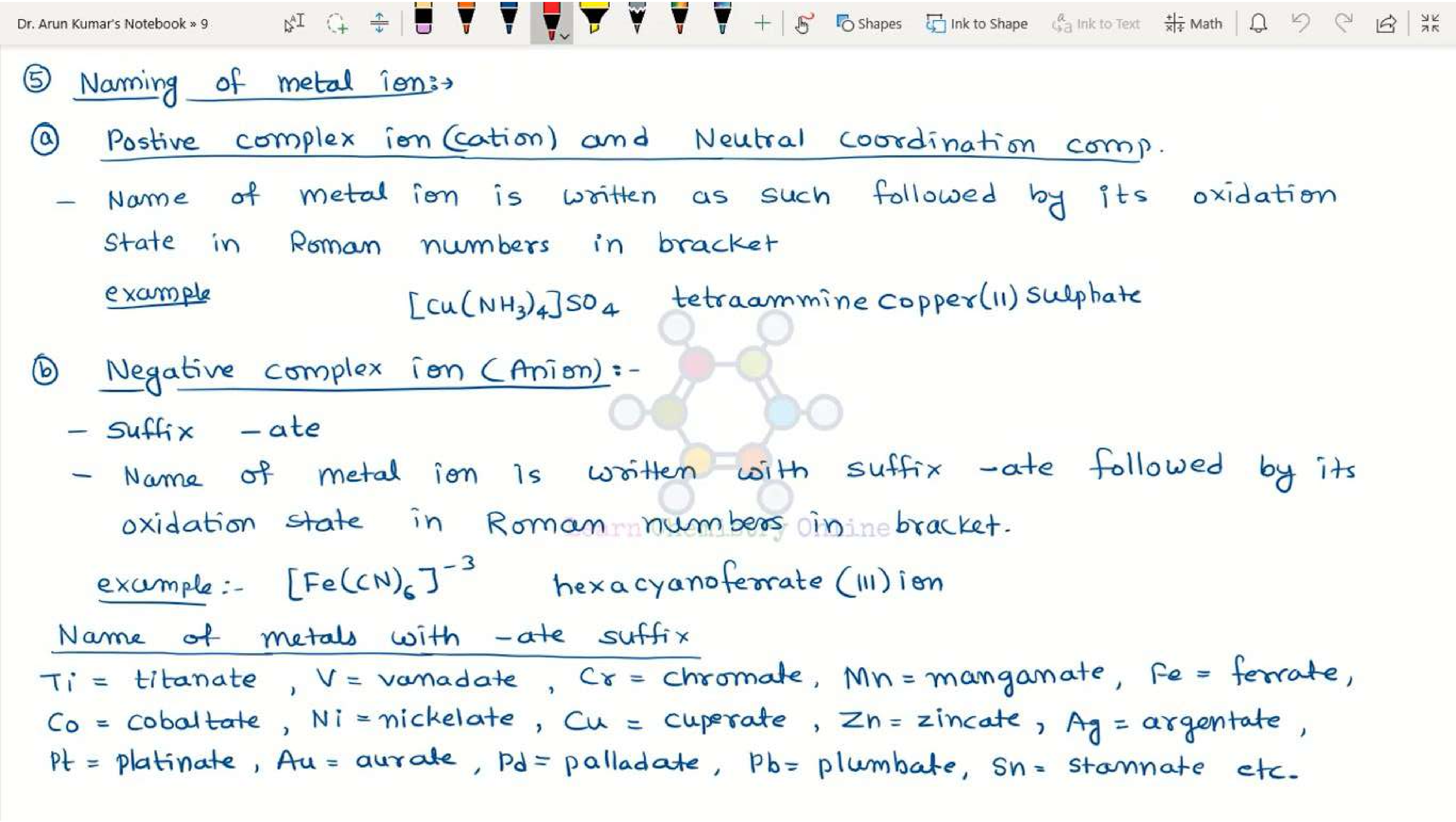
ⓓ If the bridging ligand bridges more than two metal atoms, then μ_3, μ_4 etc is used before the name of bridging ligand.

- μ_3 & μ_4 indicates no. of metal atoms

example $[Be_4O(CH_3COO)_6]$ μ_4-oxo-hexa-μ-acetato tetraberyllium (II)

(ix) Abrreviation used for complicated ligands:-

(en)	etylenediamine
(dien)	diethylene triamine
(trien)	triethylene tetramine
$(edta^{3-})$	ethylendiamine triacetato
$(acac^{-})$	acetylacetonato
(dmg^{-})	dimethyl glyoximato
$(edta^{4-})$	ethylenediaminetetraacetato
(gly^{-})	glycinato
(phen)	1,10 - phenathroline
(py)	pyridyl
(tu)	thiourea
(dipy)	dipyridyl
(tripy)	tripyridyl
(ox^{2-})	oxalato



⑤ Naming of metal ion:→

ⓐ Postive complex ion (cation) and Neutral coordination comp.

- Name of metal ion is written as such followed by its oxidation state in Roman numbers in bracket

example $[Cu(NH_3)_4]SO_4$ tetraammine copper(II) sulphate

ⓑ Negative complex ion (Anion):-

- suffix -ate
- Name of metal ion is written with suffix -ate followed by its oxidation state in Roman numbers in bracket.

example:- $[Fe(CN)_6]^{-3}$ hexacyanoferrate (III) ion

Name of metals with -ate suffix

Ti = titanate , V = vanadate , Cr = chromate , Mn = manganate , Fe = ferrate ,
Co = cobaltate , Ni = nickelate , Cu = cuperate , Zn = zincate , Ag = argentate ,
Pt = platinate , Au = aurate , Pd = palladate , Pb = plumbate , Sn = stannate etc.

ⓒ If the complex contains H+ as a cation, then suffix -ic is used for metal atom.

example $H_4[Pt(CN)_6]$ hexacyanoplatinic(II) acid

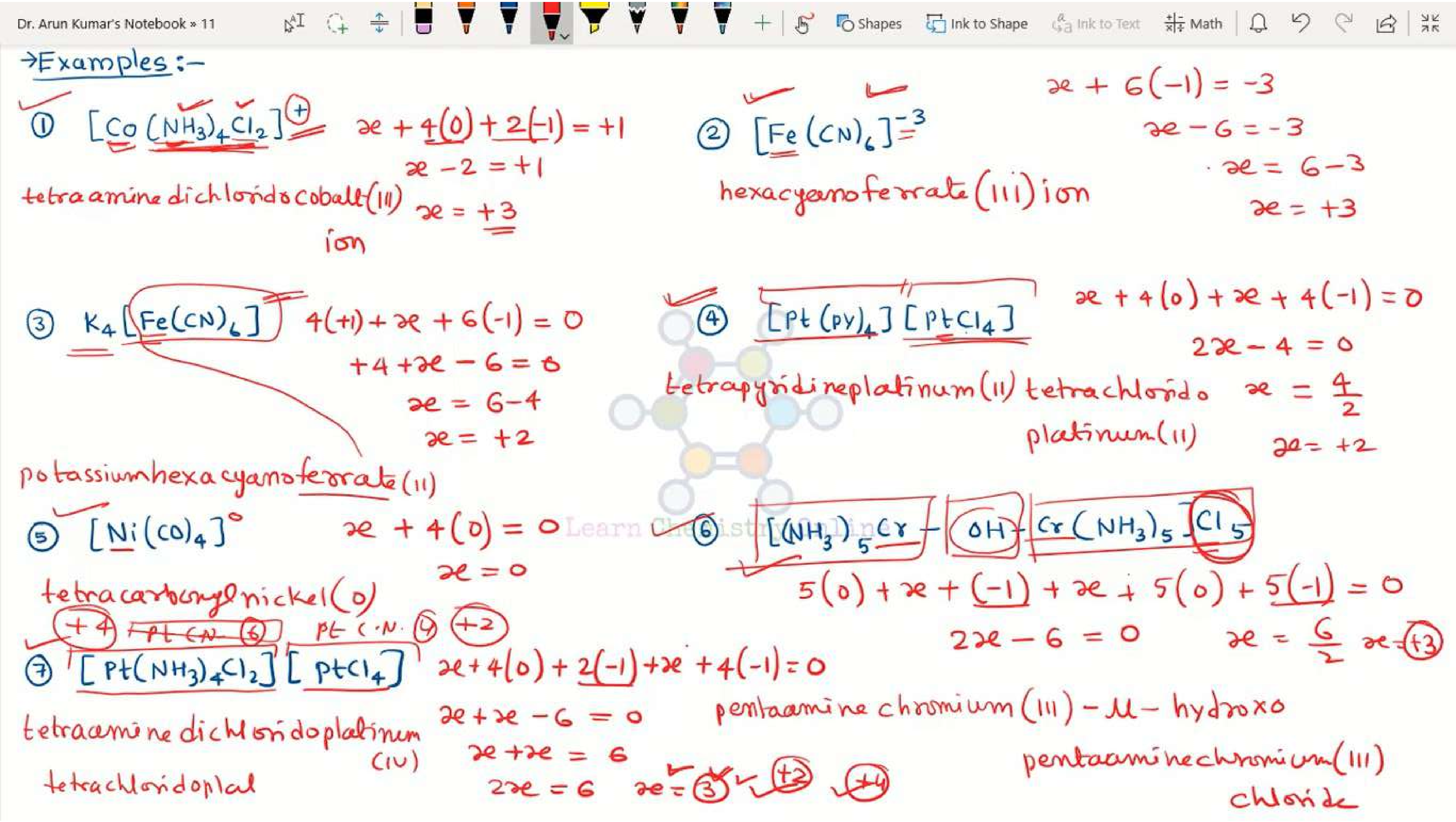
ⓓ **Naming of Geometrical isomers** :- these isomers are named as cis or trans on the basis of position of ligands

ⓔ **Naming of optical isomers** :→ prefix d or (+) for dextro
l or (-) for laevo

⑥ **Naming of counter ion or simple ion**:-

- no. of counter ion is not shown in nomenclature whether it is cation or anion

example :- $K_3[Fe(CN)_6]$



→Examples :-

① $[Co(NH_3)_4Cl_2]^{+}$

$x + 4(0) + 2(-1) = +1$

$x - 2 = +1$

$x = +3$

tetraaminedichloridocobalt(III) ion

② $[Fe(CN)_6]^{-3}$

$x + 6(-1) = -3$

$x - 6 = -3$

$x = 6 - 3$

$x = +3$

hexacyanoferrate(III) ion

③ $K_4[Fe(CN)_6]$

$4(+1) + x + 6(-1) = 0$

$+4 + x - 6 = 0$

$x = 6 - 4$

$x = +2$

potassiumhexacyanoferrate(II)

④ $[Pt(py)_4][PtCl_4]$

$x + 4(0) + x + 4(-1) = 0$

$2x - 4 = 0$

$x = \frac{4}{2}$

$x = +2$

tetrapyridineplatinum(II) tetrachlorido platinum(II)

⑤ $[Ni(CO)_4]^{0}$

$x + 4(0) = 0$

$x = 0$

tetracarbonylnickel(0)

⑥ $[(NH_3)_5Cr - OH - Cr(NH_3)_5]Cl_5$

$5(0) + x + (-1) + x + 5(0) + 5(-1) = 0$

$2x - 6 = 0$

$x = \frac{6}{2}$ $x = +3$

pentaamine chromium(III) – μ – hydroxo pentaaminechromium(III) chloride

+4 ~~Pt CN 6~~ Pt C.N. 4 +2

⑦ $[Pt(NH_3)_4Cl_2][PtCl_4]$

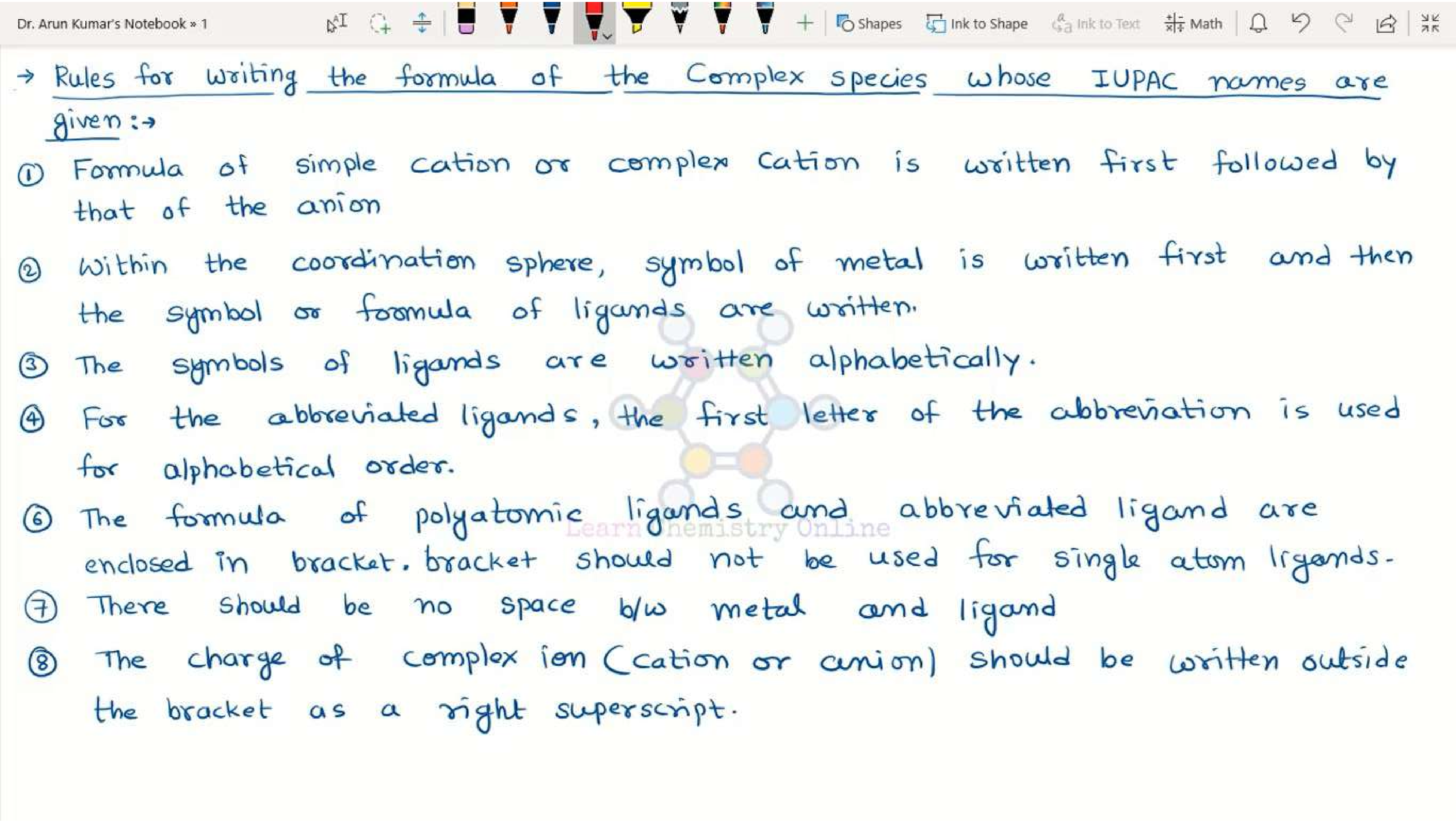
$x + 4(0) + 2(-1) + x + 4(-1) = 0$

$x + x - 6 = 0$

$x + x = 6$

$2x = 6$ $x = 3$ +2 +4

tetraamminedichloridoplatinum (IV) tetrachloridoplat



→ Rules for writing the formula of the Complex species whose IUPAC names are given :→

① Formula of simple cation or complex cation is written first followed by that of the anion

② Within the coordination sphere, symbol of metal is written first and then the symbol or formula of ligands are written.

③ The symbols of ligands are written alphabetically.

④ For the abbreviated ligands, the first letter of the abbreviation is used for alphabetical order.

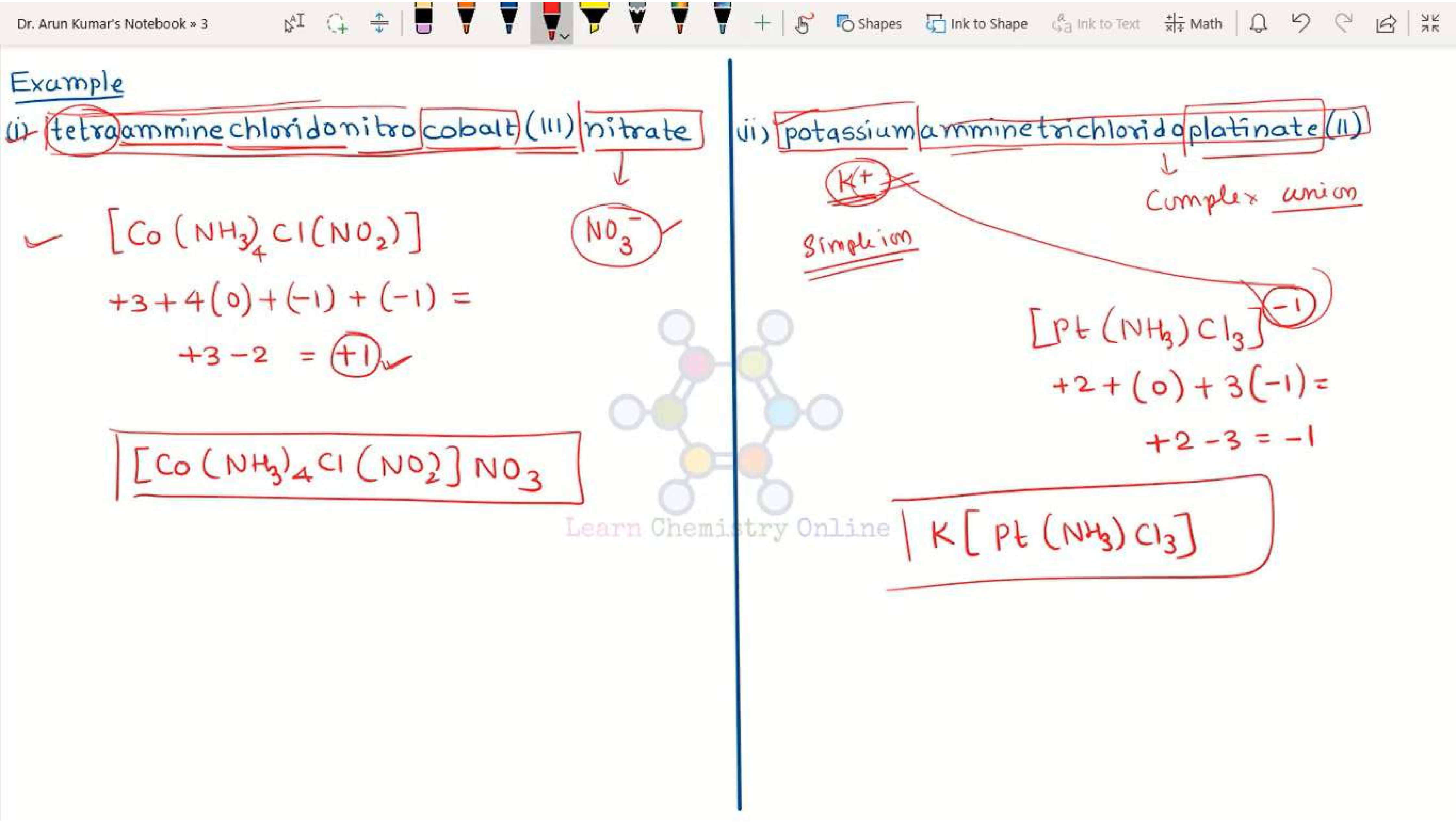
⑥ The formula of polyatomic ligands and abbreviated ligand are enclosed in bracket. bracket should not be used for single atom ligands.

⑦ There should be no space b/w metal and ligand

⑧ The charge of complex ion (cation or anion) should be written outside the bracket as a right superscript.

⑨ The no. of cations and anions should be calculated on the basis of the fact that the total +ve charge must be equal to total -ve charge. since the complex is electrically neutral.

⑩ Charge on the complex ion is equal to sum of the charge on metal ion and charge on the ligands.



Example

(i) tetraamminechloridonitrocobalt(III)nitrate

$\to NO_3^-$ ✓

✓ $[Co(NH_3)_4Cl(NO_2)]$

$+3 + 4(0) + (-1) + (-1) =$

$+3 - 2 = \boxed{+1}$ ✓

$$\boxed{[Co(NH_3)_4Cl(NO_2)]NO_3}$$

(ii) potassiumamminetrichloridoplatinate(II)

K^+

Simple ion

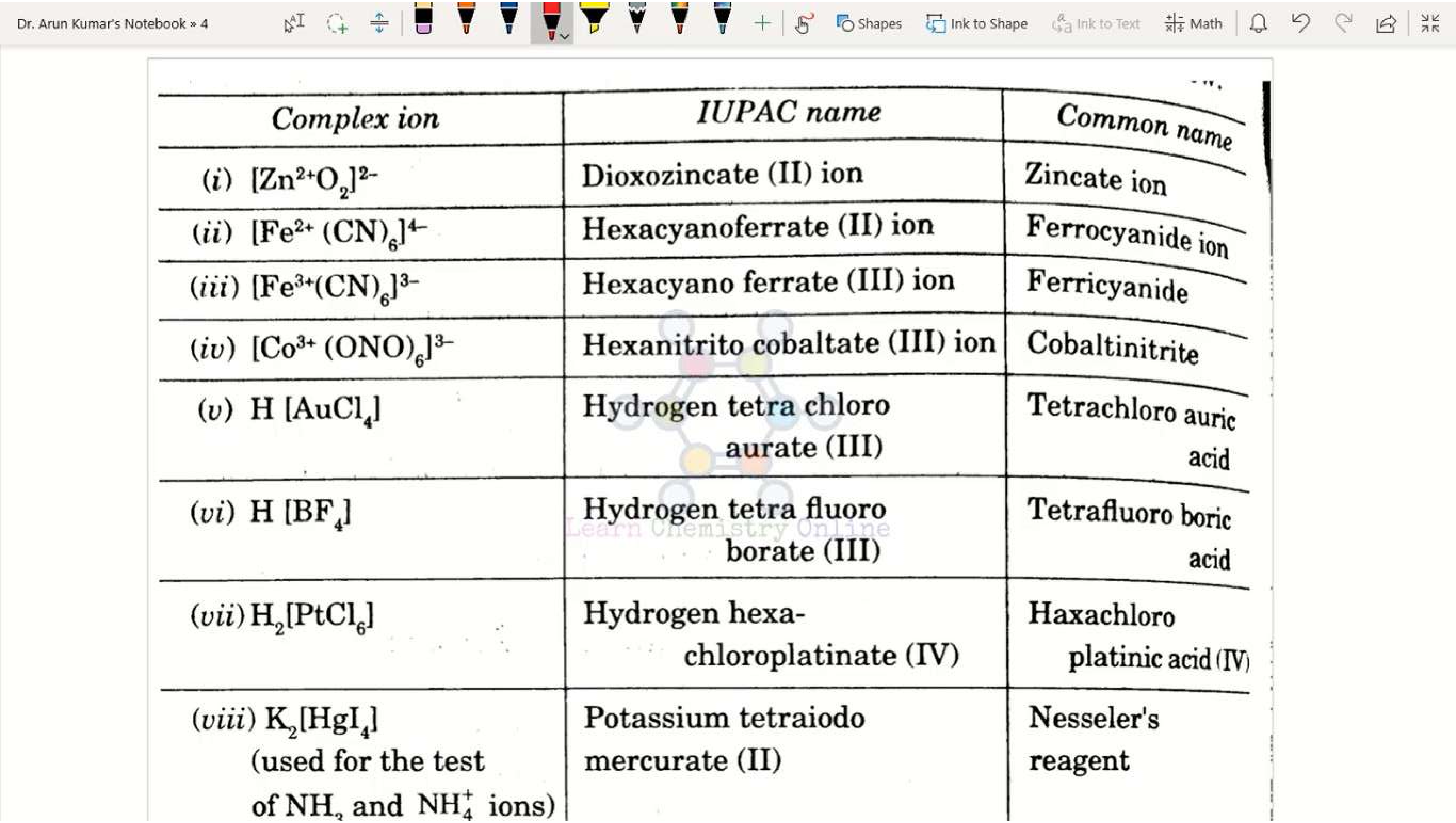
$\to$ Complex anion

$[Pt(NH_3)Cl_3]^{-1}$

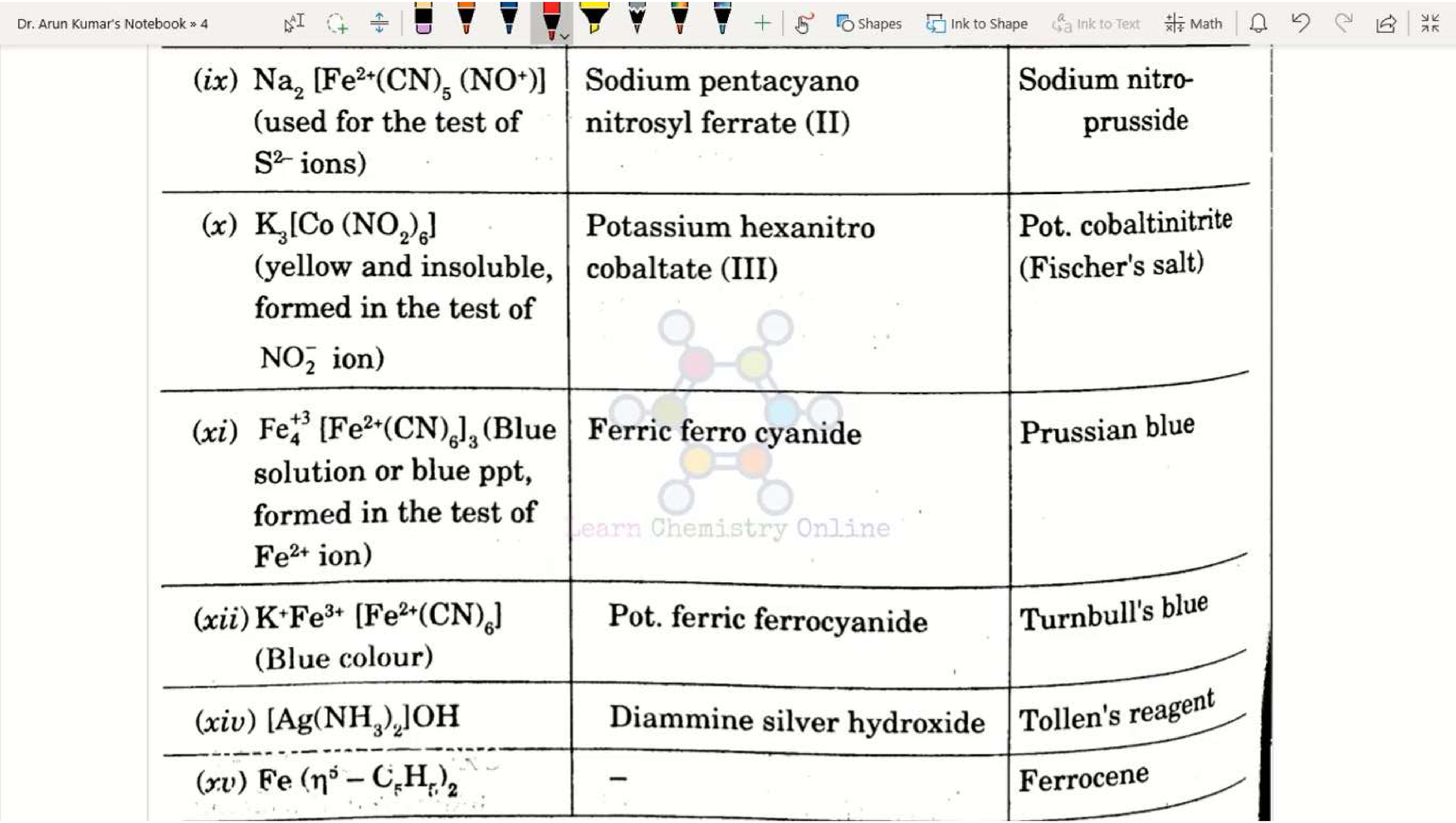
$+2 + (0) + 3(-1) =$

$+2 - 3 = -1$

$$\boxed{K[Pt(NH_3)Cl_3]}$$



Complex ion	*IUPAC name*	*Common name*
(*i*) $[Zn^{2+}O_2]^{2-}$	Dioxozincate (II) ion	Zincate ion
(*ii*) $[Fe^{2+}(CN)_6]^{4-}$	Hexacyanoferrate (II) ion	Ferrocyanide ion
(*iii*) $[Fe^{3+}(CN)_6]^{3-}$	Hexacyano ferrate (III) ion	Ferricyanide
(*iv*) $[Co^{3+}(ONO)_6]^{3-}$	Hexanitrito cobaltate (III) ion	Cobaltinitrite
(*v*) $H[AuCl_4]$	Hydrogen tetra chloro aurate (III)	Tetrachloro auric acid
(*vi*) $H[BF_4]$	Hydrogen tetra fluoro borate (III)	Tetrafluoro boric acid
(*vii*) $H_2[PtCl_6]$	Hydrogen hexachloroplatinate (IV)	Haxachloro platinic acid (IV)
(*viii*) $K_2[HgI_4]$ (used for the test of NH_3 and NH_4^+ ions)	Potassium tetraiodo mercurate (II)	Nesseler's reagent



(*ix*) $Na_2\,[Fe^{2+}(CN)_5\,(NO^+)]$ (used for the test of S^{2-} ions)	Sodium pentacyano nitrosyl ferrate (II)	Sodium nitro-prusside
(*x*) $K_3[Co\,(NO_2)_6]$ (yellow and insoluble, formed in the test of NO_2^- ion)	Potassium hexanitro cobaltate (III)	Pot. cobaltinitrite (Fischer's salt)
(*xi*) $Fe_4^{+3}\,[Fe^{2+}(CN)_6]_3$ (Blue solution or blue ppt, formed in the test of Fe^{2+} ion)	Ferric ferro cyanide	Prussian blue
(*xii*) $K^+Fe^{3+}\,[Fe^{2+}(CN)_6]$ (Blue colour)	Pot. ferric ferrocyanide	Turnbull's blue
(*xiv*) $[Ag(NH_3)_2]OH$	Diammine silver hydroxide	Tollen's reagent
(*xv*) $Fe\,(\eta^5 - C_5H_5)_2$	–	Ferrocene

→ Werner's theory of coordination compounds :→

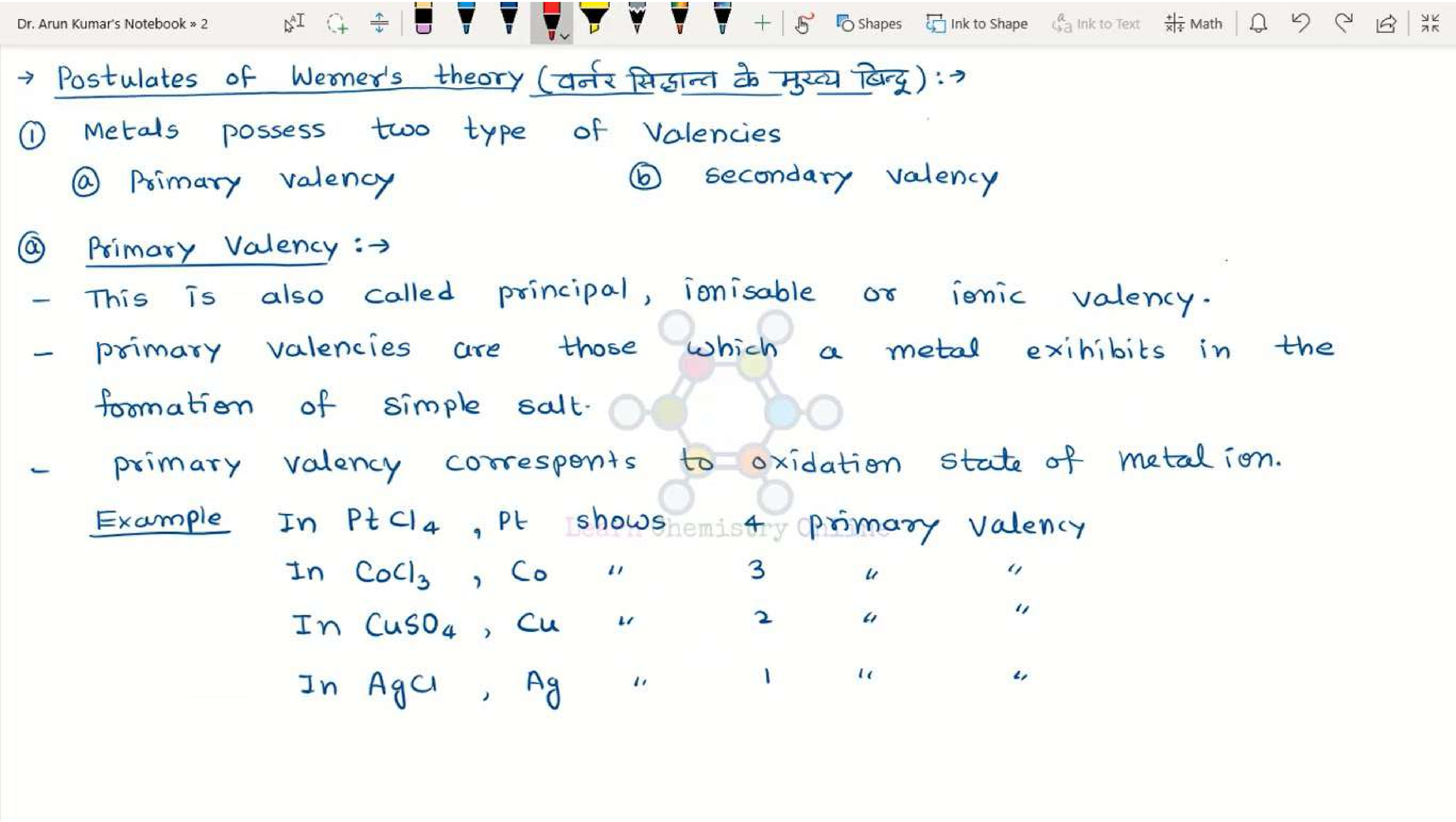
संकुल यौगिकों का वर्नर सिद्धान्त :→

- This theory was given by Werner in 1893 to explain nature of bonding and structure of coordination compounds.
- Werner isolated different complex compounds from the reaction of Cobalt chloride and ammonia. These compounds are called cobalt ammines.

$CoCl_3 \cdot 6NH_3$	$CoCl_3 \cdot 5NH_3$	$CoCl_3 \cdot 4NH_3$	$CoCl_3 \cdot 4NH_3$	$CoCl_3 \cdot 3NH_3$
Yellow	Purple	Violet	Green	Blue green

Violet, Green → Geometrical or cis-trans isomers

- Werner studied the properties of these compounds and many other such compounds in detail. Based on these properties, he proposed Werner's theory of coordination compounds.



→ **Postulates of Werner's theory (वर्नर सिद्धान्त के मुख्य बिन्दु) :→**

① Metals possess two type of Valencies

ⓐ Primary valency ⓑ secondary valency

ⓐ **Primary Valency :→**

- This is also called principal, ionisable or ionic valency.
- primary valencies are those which a metal exihibits in the formation of simple salt.
- primary valency correspents to oxidation state of metal ion.

Example In $PtCl_4$, Pt shows 4 primary valency
In $CoCl_3$, Co " 3 " "
In $CuSO_4$, Cu " 2 " "
In AgCl , Ag " 1 " "

ⓑ **Secondary valency :→**

- This is also called non-ionisable or non-ionic valency.
- Secondary valencies are those which a metal coordinated with ligands in the formation of it complex ion.
- Secondary valency is also termed as coordination number (C.N.) of the metal ion.

example: In $[Pt(NH_3)_6]Cl_4$, C.N. of Pt^{+4} is 6

In $[Cu(NH_3)_4]SO_4$, C.N. of Cu^{+2} is 4

In $[Ag(NH_3)_2]Cl$, C.N. of Ag^{+1} is 2

② Every metal atom has tendency to satisfy both its primary and secondary valencies. primary valency is satisfied by negative ions whereas secondary valencies are satisfied by negative ions or neutral molecule (ligands). In certain cases a negative ion may satisfy both type of valencies.

③ The secondary valencies (i.e. ligands) are always directed towards the fixed position in space and this bond leads to definite geometry of the coordination compounds.

Thus, secondary valencies determine the stereochemistry of the complex.

<u>example</u>

Sec. valencies of metal ion	Geometry
4	Tetrahedral or square planar
6	Octahedral

④ While writing the structure of coordination compound according to Werner's theory, the primary valencies are represented by broken lines (- - - -) and secondary valencies are shown by solid lines (——).

→ Explaination of structure of cobalt (III) amines on the basis of Werner's theory :→

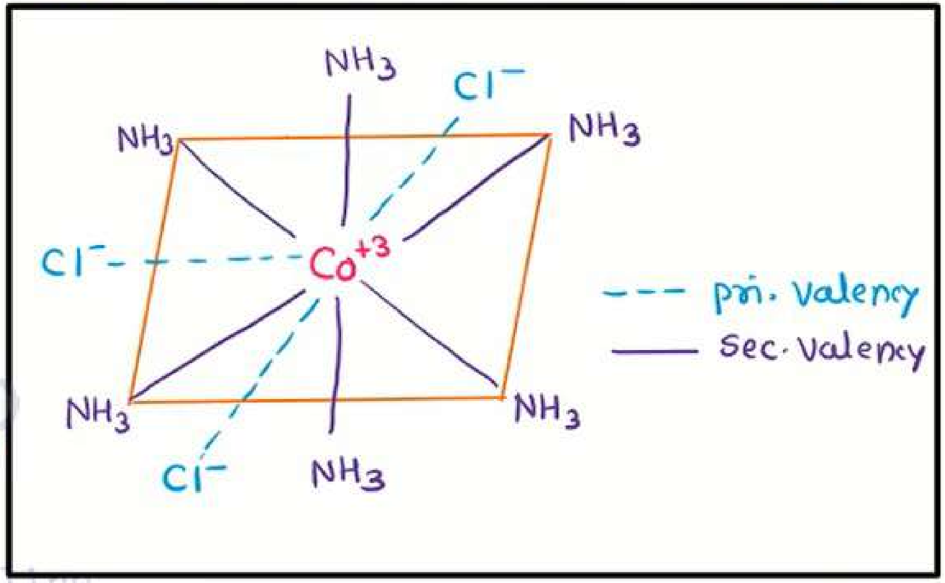
- The reaction between $CoCl_3$ and NH_3 gives $CoCl_3 \cdot 6NH_3$, $CoCl_3 \cdot 5H_2O$, $CoCl_3 \cdot 4H_2O$ and $CoCl_3 \cdot 3H_2O$.
- on the basis of his theory werners explained the structure of these Cobalt ammines
- In these cobalt amines -

  primary valencies(---) of Cobalt → 3 → satisfied by three Cl^- ions

  Secondary valencies(—) of Cobalt → 6 → Satisfied by NH_3 or both NH_3 & Cl^-
- Since Coordination no (sec. valency) of Co is 6, all compounds have octahedral geometry

(i) $CoCl_3 \cdot 6NH_3$:→

- Primary valency of Co is 3 and satisfied with 3 Cl^- and hence represented by broken lines (----)



- Reaction with aqueous sol. of $AgNO_3$.

$$CoCl_3 \cdot 6NH_3 \longrightarrow [Co \cdot 6NH_3]^{+3} + 3Cl^-$$

$$3Ag^+ + 3Cl^- \rightarrow 3AgCl \text{ (white ppt)}$$

- The precipitation of $3Cl^-$ indicates that $3Cl^-$ ions are outside the coordination sphere and six NH_3 are inside the coordination sphere.

- Thus structure of this molecule is written as $[Co \cdot 6NH_3]Cl_3$ or $[Co(NH_3)_6]Cl_3$
- This structure shows that secondary valency of Co atom is equal to 6 and statisfied with 6 NH_3.
- The attachment of NH_3 is shown by solid lines.

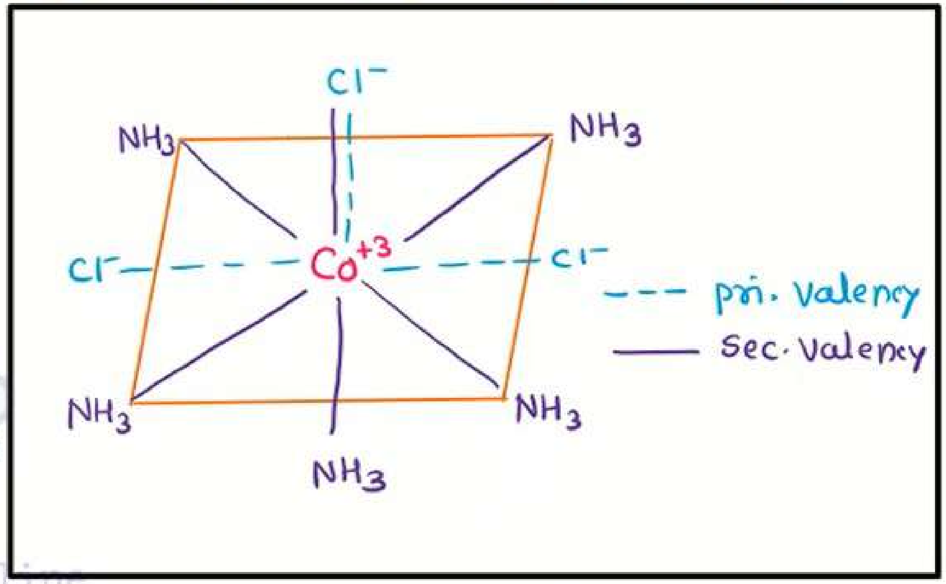
(ii) $CoCl_3 \cdot 5NH_3$:→

- Primary valency of Co is 3 and satisfied with 3 Cl^- and hence represented by broken lines (- - - -)
- Reaction with aqueous sol. of $AgNO_3$.

$$CoCl_3 \cdot 5NH_3 \longrightarrow [CoCl \cdot 5NH_3]^{+2} + 2Cl^-$$

$$2Ag^+ + 2Cl^- \rightarrow 2AgCl \text{ (White ppt)}$$

- The precipitation of 2 Cl^- indicates that 2 Cl^- ions are outside the coordination sphere and 1 Cl^- & 5 NH_3 are inside the coordination sphere.



- Thus structure of this molecule is written as $[CoCl \cdot 5NH_3]Cl_2$ or $[Co(NH_3)_5Cl]Cl_2$
- This structure shows that secondary valency of Co atom is equal to 6 and statisfied with 5 NH_3 and 1 Cl^- ion.
- The attachment of NH_3 is shown by solid lines and attachment of 1 Cl^- is shown by both lines i.e. (═ - - - ═)

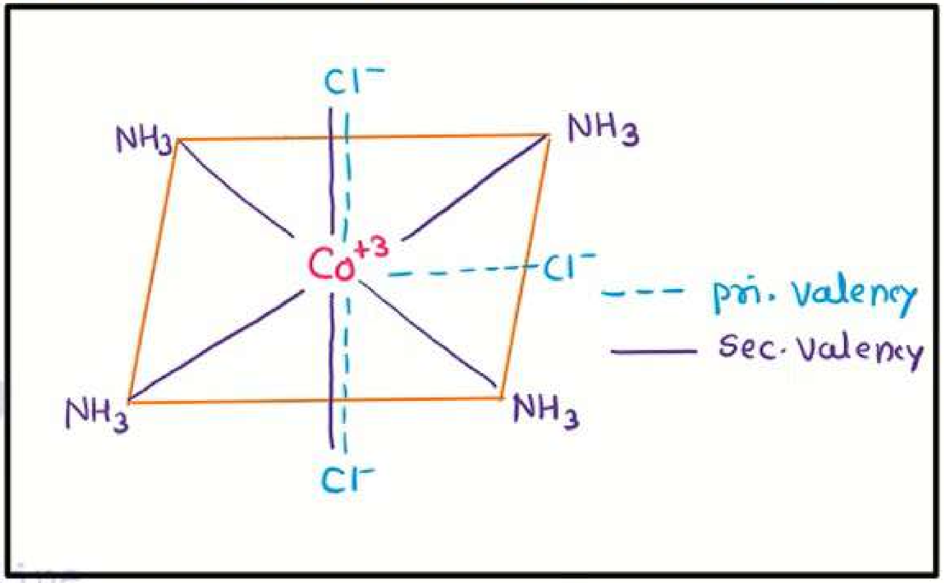
(iii) $CoCl_3 \cdot 4NH_3$:→

- Primary valency of Co is 3 and satisfied with 3 Cl^- and hence represented by broken lines (- - - -)
- Reaction with aqueous sol. of $AgNO_3$.

$$CoCl_3 \cdot 4NH_3 \longrightarrow [CoCl_2 \cdot 4NH_3]^+ + Cl^-$$

$$Ag^+ + Cl^- \rightarrow AgCl \text{ (white ppt)}$$

- The precipitation of 1 Cl^- indicates that 1 Cl^- ions are outside the coordination sphere and 2Cl^- & 4NH_3 are inside the coordination sphere.



- Thus structure of this molecule is written as $[CoCl_2 \cdot 4NH_3]Cl$ or $[Co(NH_3)_4Cl_2]Cl$.
- This structure shows that secondary valency of Co atom is equal to 6 and statisfied with 4 NH_3 and 2 Cl^- ion.
- The attachment of NH_3 is shown by solid lines and attachment of 2 Cl^- is shown by both lines i.e. (═ ═ ═)

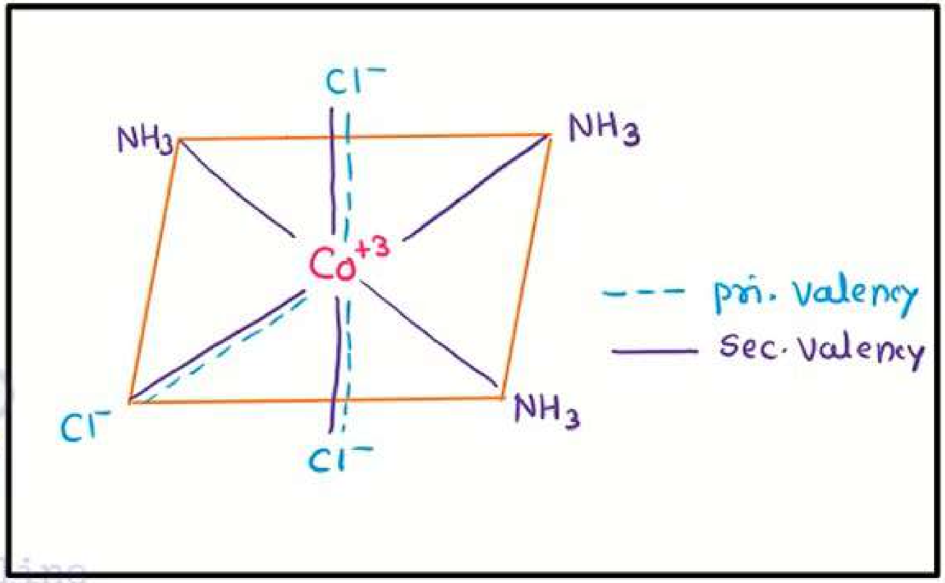
(iv) $CoCl_3 \cdot 3NH_3$:→

- Primary valency of Co is 3 and satisfied with $3Cl^-$ and hence represented by broken lines (- - - -)
- Reaction with aqueous sol. of $AgNO_3$.

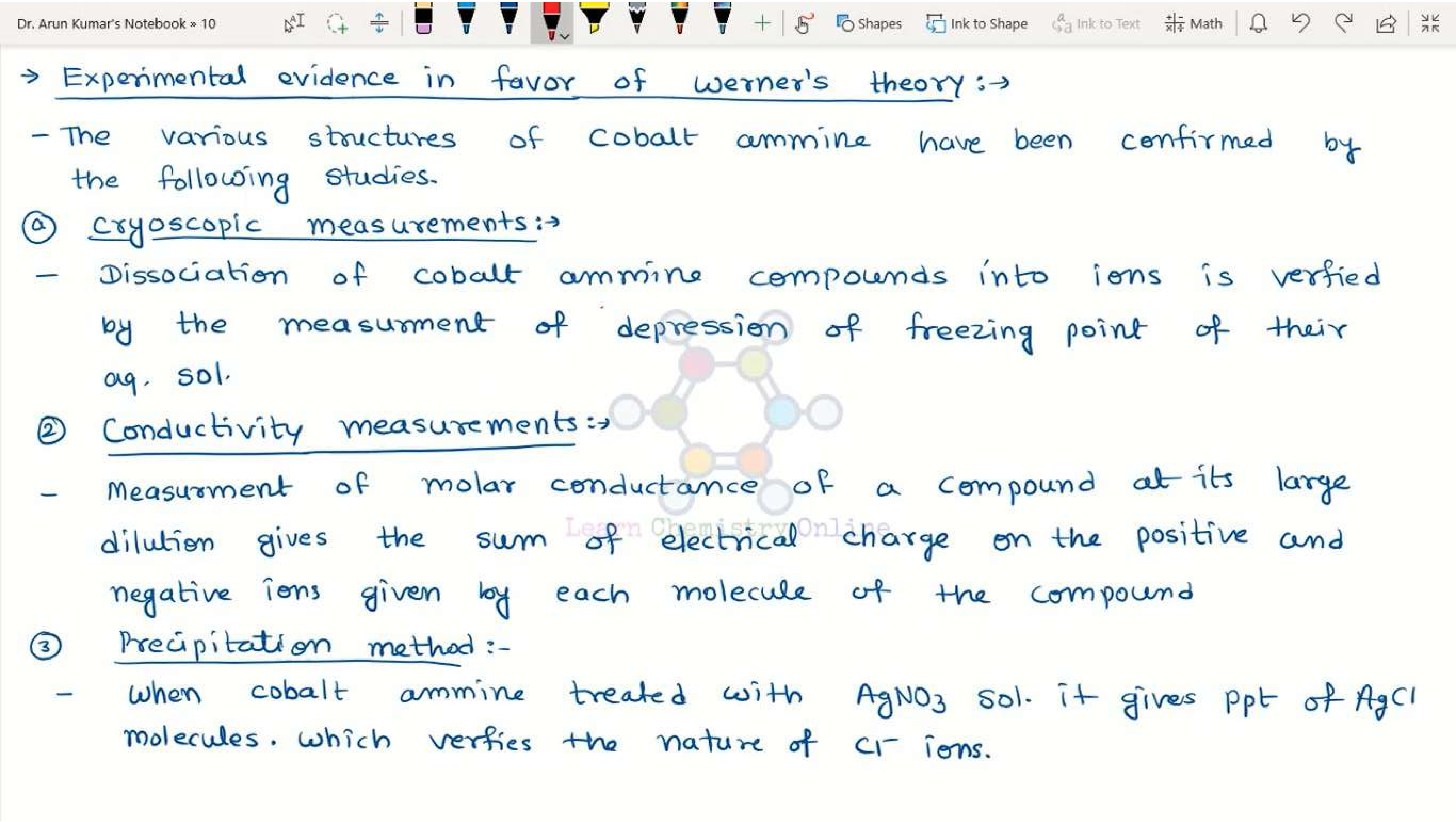
$$CoCl_3 \cdot 3NH_3 \longrightarrow \text{No dissociation}$$

No ppt with $AgNO_3$

- NO precipitation of Cl^- indicates that no Cl^- ions are outside the coordination sphere and $3Cl^-$ & $3NH_3$ are inside the coordination sphere.



- Thus structure of this molecule is written as $[CoCl_3 \cdot 3NH_3]^0$ or $[Co(NH_3)_3Cl_3]^0$
- This structure shows that secondary valency of Co atom is equal to 6 and statisfied with $3NH_3$ and $3Cl^-$ ion.
- The attachment of NH_3 is shown by solid lines and attachment of $3Cl^-$ is shown by bot lines i.e. ($\overset{\text{-----}}{\underline{\text{-----}}}$)



→ Experimental evidence in favor of werner's theory :→

- The various structures of cobalt ammine have been confirmed by the following studies.

ⓐ **Cryoscopic measurements :→**

- Dissociation of cobalt ammine compounds into ions is verfied by the measurment of depression of freezing point of their aq. sol.

② **Conductivity measurements :→**

- Measurment of molar conductance of a compound at its large dilution gives the sum of electrical charge on the positive and negative ions given by each molecule of the compound

③ **Precipitation method :-**

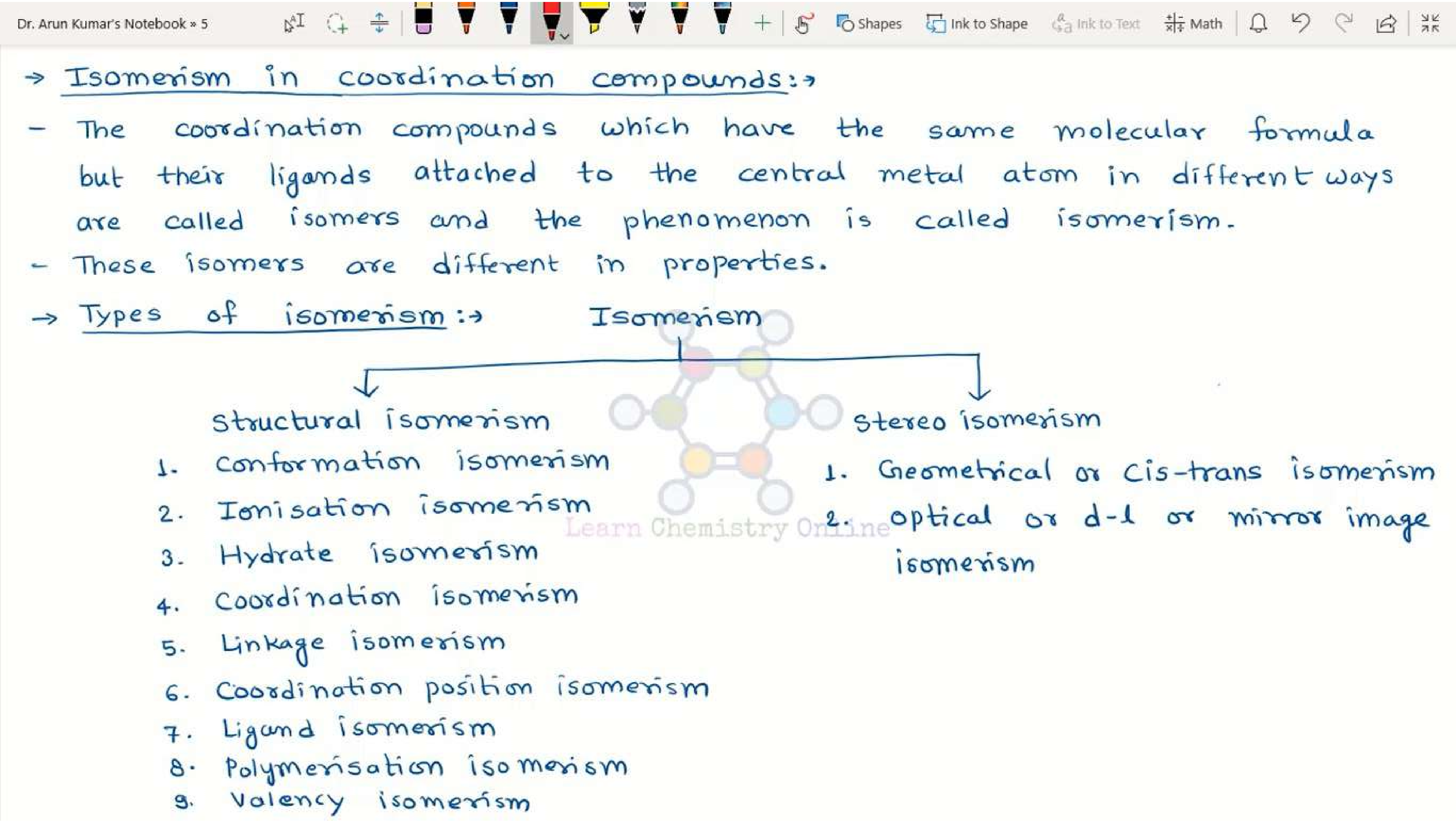
- When cobalt ammine treated with $AgNO_3$ sol. it gives ppt of AgCl molecules. which verfies the nature of Cl^- ions.

→ Limitations of Werner's theory :→

① This theory does not explain that, why some elements form coordination compounds while others not.

② This theory does not explain that why the coordination sphere has definite geometry

③ This theory unable to explain magnetic and optical properties of coordination compounds



→ Isomerism in coordination compounds :→

- The coordination compounds which have the same molecular formula but their ligands attached to the central metal atom in different ways are called isomers and the phenomenon is called isomerism.
- These isomers are different in properties.

→ Types of isomerism :→

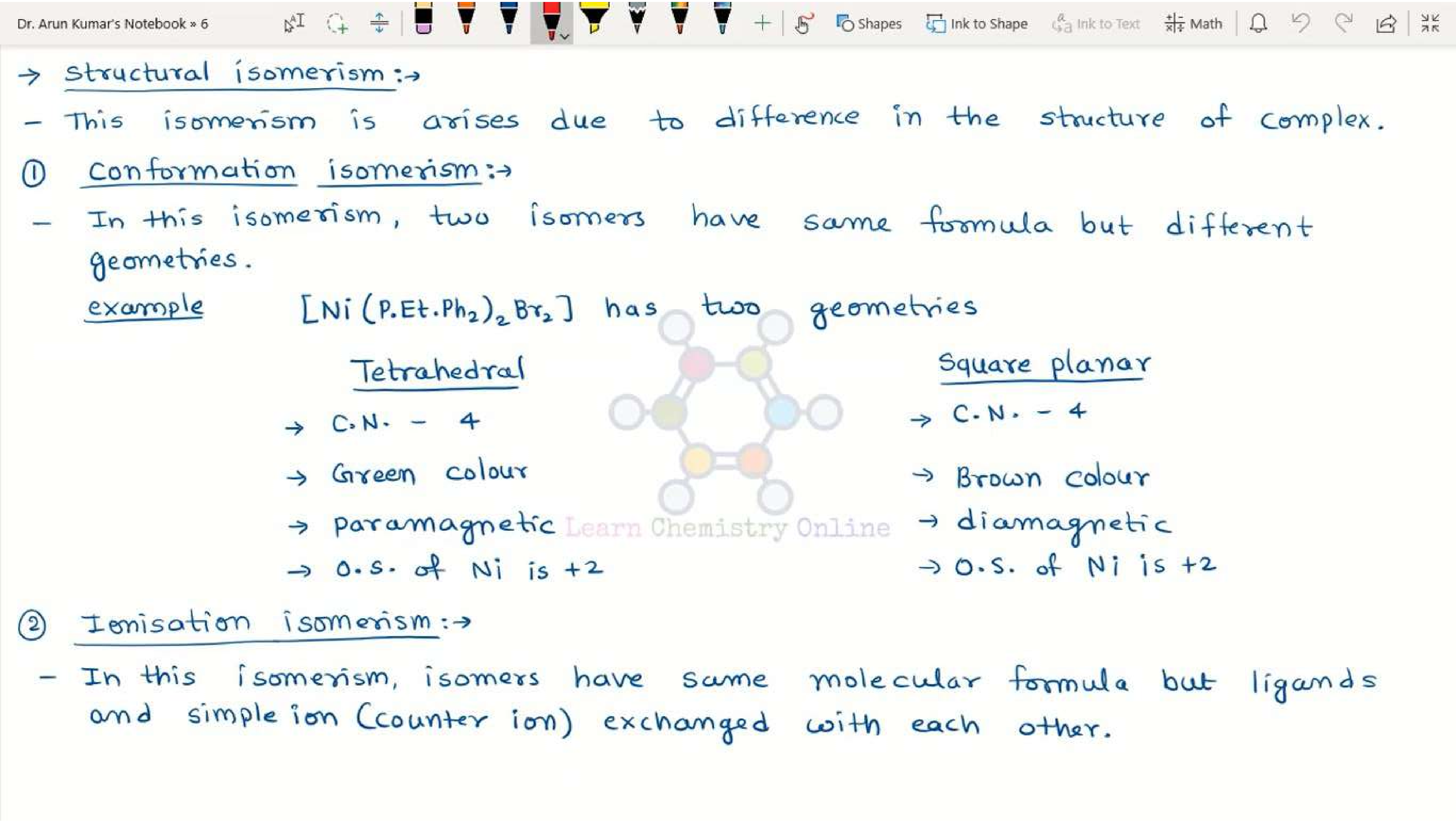
Isomerism

Structural isomerism

1. Conformation isomerism
2. Ionisation isomerism
3. Hydrate isomerism
4. Coordination isomerism
5. Linkage isomerism
6. Coordination position isomerism
7. Ligand isomerism
8. Polymerisation isomerism
9. Valency isomerism

Stereo isomerism

1. Geometrical or Cis-trans isomerism
2. optical or d-l or mirror image isomerism



→ **Structural isomerism :→**

- This isomerism is arises due to difference in the structure of complex.

① **Conformation isomerism :→**

- In this isomerism, two isomers have same formula but different geometries.

example $[Ni(P.Et.Ph_2)_2Br_2]$ has two geometries

Tetrahedral	Square planar
→ C.N. – 4	→ C.N. – 4
→ Green colour	→ Brown colour
→ paramagnetic	→ diamagnetic
→ O.S. of Ni is +2	→ O.S. of Ni is +2

② **Ionisation isomerism :→**

- In this isomerism, isomers have same molecular formula but ligands and simple ion (counter ion) exchanged with each other.

Example:- (i) $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5(SO_4)]Br$

(ii) $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

- These isomers have different properties due to different behaviour in aqueous solution.
- Ionisation isomers can be detected by the determination of their conductance in solution.

③ Hydrate isomerism:→

- This isomerism is similar to ionisation isomerism.
- This isomerism arises when H_2O molecules acting as ligands are replaced by the counter ion.

Example:- $CrCl_3 \cdot 6H_2O$ exists in three hydrate isomers.

$[Cr(H_2O)_6]Cl_3$	$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$	$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$
Violet	blue green	green

④ Coordination Isomerism:→

- This type of isomerism is shown by those complex compounds which are composed of complex cation and complex anion.
- This isomerism arises when some or all ligands of both coordination sphere are interchanged with each other
- In these pairs the central metal atom in the two coordination sphere may be same or different.

example:-

(i) $[Cr(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_4(CN)_2][Cr(NH_3)_2(CN)_4]$

(ii) $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

⑤ Linkage Isomerism:→

- Linkage isomerism is shown by those coordination compounds which contain ambidentate ligands.
- This isomerism arises when ambidentate ligand linking to metal atom through two different donor atom and gives two different compounds.

example:-

$[Co(NH_3)_5NO_2]^{+2}$

- NO_2^- linked to Co with N-atom

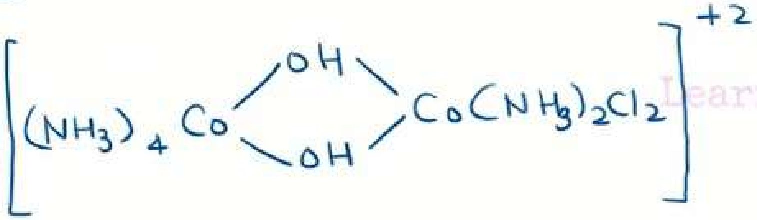
$[Co(NH_3)_5(ONO)]^{+2}$

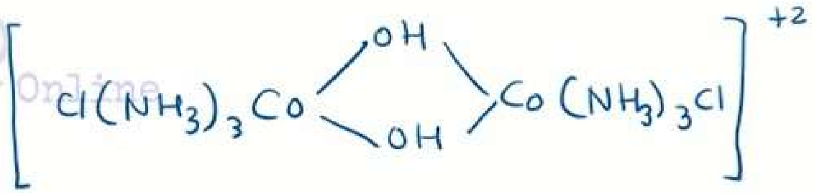
- NO_2^- linked to Co with O-atom

⑥ Coordination Position Isomerism:→

- This isomerism is shown by those complexes which contain bridging ligands.
- This arises when the non bridging ligands are differently placed round the central metal atom

example:-

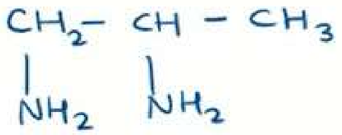




⑦ Ligand isomerism :→

- There are certain ligands which exist as isomer. when such ligands get Coordinated with metal ion, two isomers are obtained. these isomers are Called ligand isomers and isomerism is called ligand isomerism.

Example



$CH_2-CH-CH_3$ (with NH_2 below CH_2 and NH_2 below CH)

propylene diamine (pn)

$NH_2-CH_2-CH_2-CH_2-NH_2$

triethylene diamine (tn)

$[Co(pn)_2Cl_2]^+$

$[Co(tn)_2Cl_2]^+$

⑧ Polymerisation isomerism :→

- This type of isomerism is found in those compounds whose formula appear to be polymers of some simple complex compound.
- All these have same ratio of different metal atoms and ligand in them.

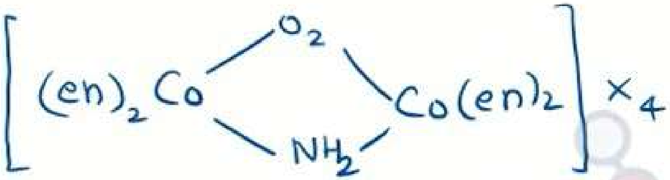
example

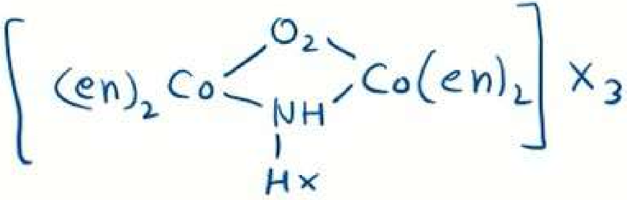
	Co^{+3}	NH_3	NO_2^-
$[Co(NH_3)_3(NO_2)_3]$	1	3	3
$[Co(NH_3)_5(NO_2)_3]_3[Co(NO_2)_6]_2$	5	15	15

⑨ Valency isomerism :→

— This isomerism arises when the ligand is held by different type of Valency bonds, sometimes primary or secondary.

- example





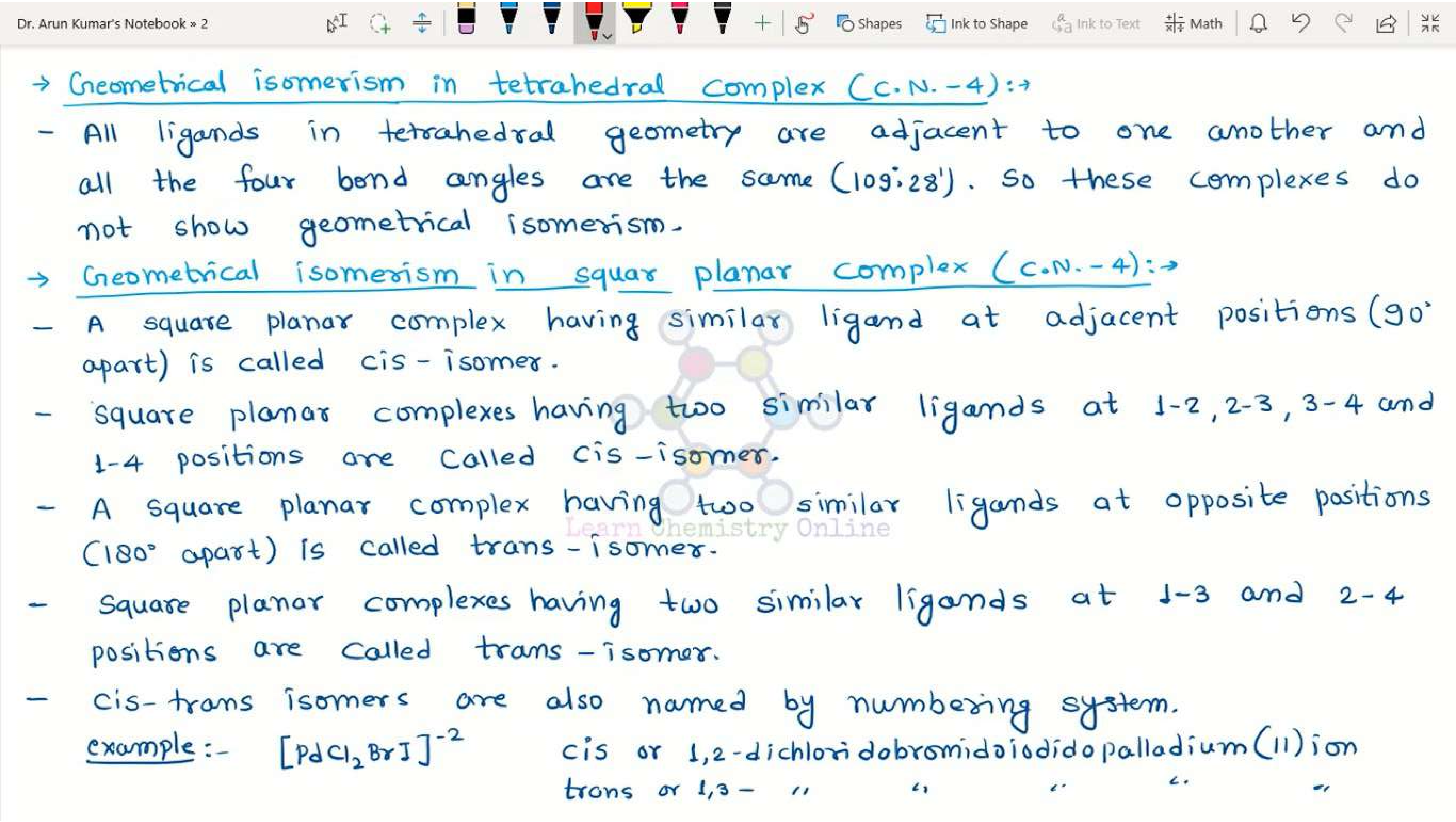
→ Geometrical isomerism in coordination compounds :→

संकुल यौगिकों में ज्यामिति समावयवता :→

- This is also called cis-trans isomerism.
- The complex compounds which have the same ligands in coordination sphere but different positions of ligands around the central atom are called geometrical isomers and phenomenon is called geometrical isomerism.
- The complex compound having two ligands occupying adjacent positions to each other is called cis-isomer.
- The complex compound having two ligands occupying opposite positions to each other is called tras-isomer.
- Geometrical isomers show different physical properties due to different positions of ligands.

- Geometrical isomerism in complex with C.N. 2 and 3:→

- these compounds do not show geometrical isomerism. because position of ligands around the metal atom is always adjocent to one another.



→ Geometrical isomerism in tetrahedral complex (C.N. – 4) :→

- All ligands in tetrahedral geometry are adjacent to one another and all the four bond angles are the same (109°28'). So these complexes do not show geometrical isomerism.

→ Geometrical isomerism in squar planar complex (C.N. – 4) :→

- A square planar complex having similar ligand at adjacent positions (90° apart) is called cis – isomer.
- Square planar complexes having two similar ligands at 1-2, 2-3, 3-4 and 1-4 positions are called cis – isomer.
- A square planar complex having two similar ligands at opposite positions (180° apart) is called trans – isomer.
- Square planar complexes having two similar ligands at 1-3 and 2-4 positions are called trans – isomer.
- cis-trans isomers are also named by numbering system.

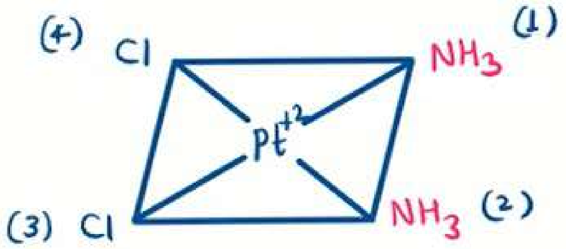
<u>example</u> :- $[PdCl_2BrI]^{-2}$ cis or 1,2-dichloridobromidoiodidopalladium(II) ion
trans or 1,3 – 〃 〃 〃 〃 〃

① Square planar complexes of $[Ma_4]$, $[Ma_3b]$ and $[Mab_3]$ type :→

- these complexes do not show geometrical isomerism. because all the possible spatial arrangement of four ligands around the metal atom is same.

② Square planar complexes of $[Ma_2b_2]$ type :→

Example $[Pt(NH_3)_2Cl_2]^0$



cis - isomer

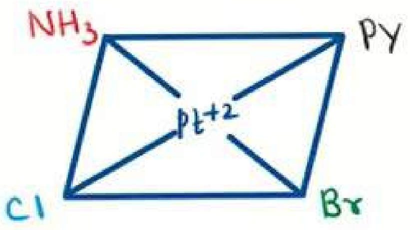
trans- isomer

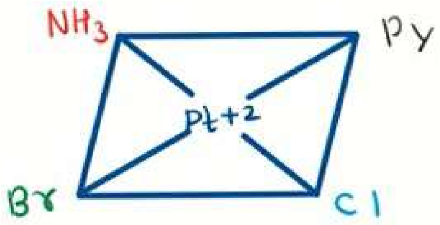
Other examples- $[Pt(Py)_2Cl_2]^0$, $[Pd(NH_3)_2(NO_2)_2]^0$ etc.

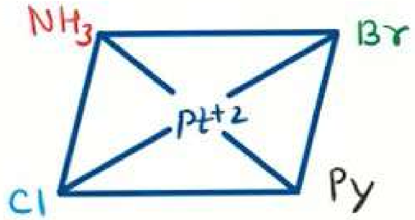
③ square planar complexes of $[Mabcd]$ type :→

Example $[Pt(NH_3)_2(Py)Cl\,Br]^0$

- three isomers can be obtained by selecting one ligand and plancing the remaining three ligands, one by one, trans to selected ligand.



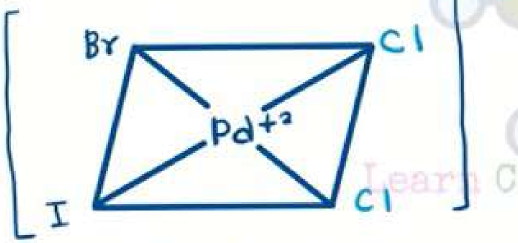




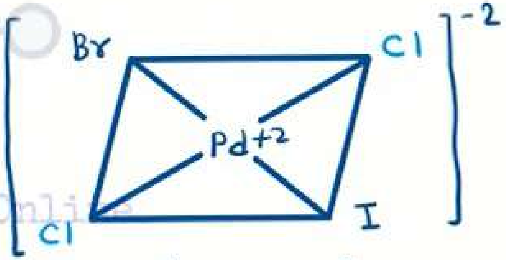
other examples:- $[Pt(NO_2)(py)(NH_3)(NH_2OH)]^+$ and $[Pt(C_2H_4)(NH_3)ClBr]$

④ Square planar complexes of $[Ma_2bc]$ type:→

Example $[PdCl_2BrI]^{-2}$



cis- isomer



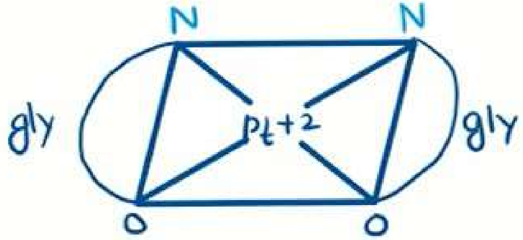
trans-isomer

other examples:- $[Pt(py)_2(NH_3)Cl]^+$

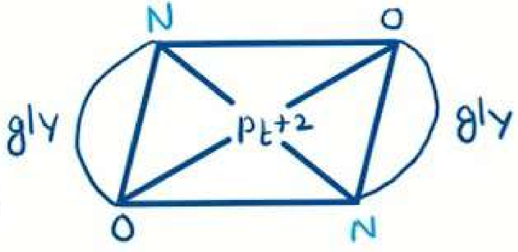
⑤ Square planar complexes of $[M(AB)_2]$ type.

AB - represents unsymmetrical bidentate ligand, in which A and B show different donor atoms.

Example:- $[Pt(gly)_2]$ gly → $NH_2 \cdot CH_2COO^-$ (donor atoms are N & O)



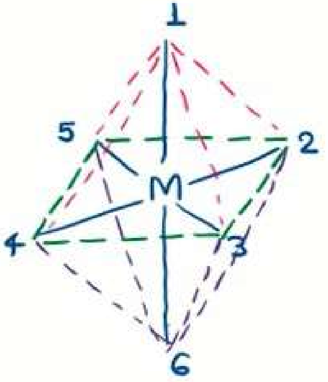
cis- isomer



trans-isomer

→ Geometrical isomerism in octahedral complexes (C.N.-6):→

- Octahedral geometry contains twelve edges
- cis-isomer → when two ligands present on any of the twelve edges (positions 1-2, 1-3, 3-6, 6-4)
- Trans-isomer → when two ligands present on straight line which passes through the centre (metal atom centre) positions -(1-6, 2-4 and 3-5)

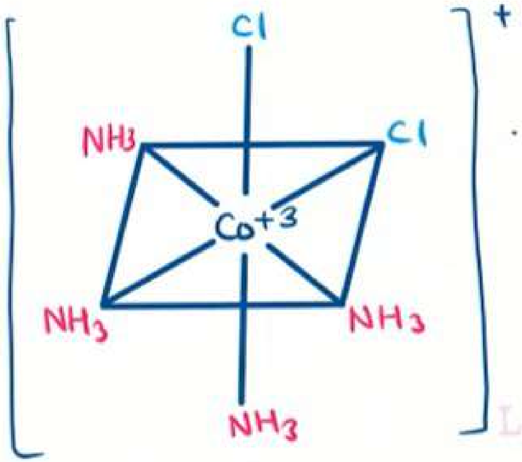


① octahedral complexes of $[Ma_6]$ and $[Ma_5b]$ tybe:→

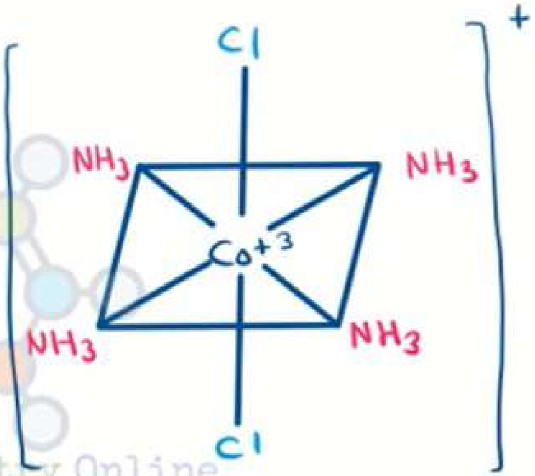
- do not show geometrical isomerism

② octahedral complexes of $[Ma_4b_2]$ type:→

- **Example** $[Co(NH_3)_4Cl_2]^+$



cis- isomer



trans-isomer

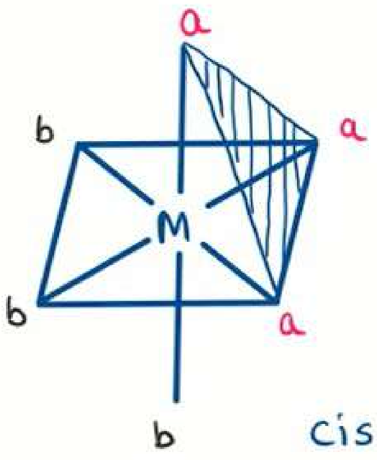
other examples :- $[Co(NH_3)_4(NO_2)_2]^+$ etc

③ octahedral complexes of $[Ma_3b_3]$ type:-

- these complexes have two type of geometrical isomers.
- octahedral geometry has 8 faces and 6 Corners (vertices)

(i) Facial or fac isomer (cis -isomer):→

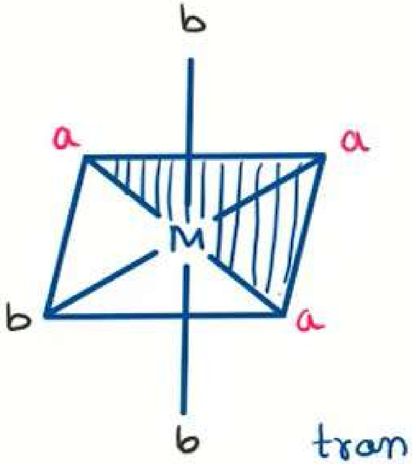
- three same ligands (a) are occupy three corners of one triangular face and other three same ligands (b) occupy of remaining 3 corners.
- This is also called cis-isomer because three a ligands are cis to each other similarly b also are cis to each other



cis (fac) isomer

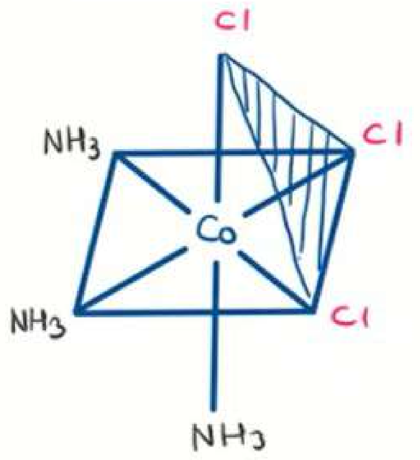
(ii) Meridional or mer-isomer (trans-isomer):→

- three same ligands (a) are in one plane and other three ligands (b) are in perpendicular plane
- a and b groups lie along the meridian of a sphere. hence called meridional or mer -isomer

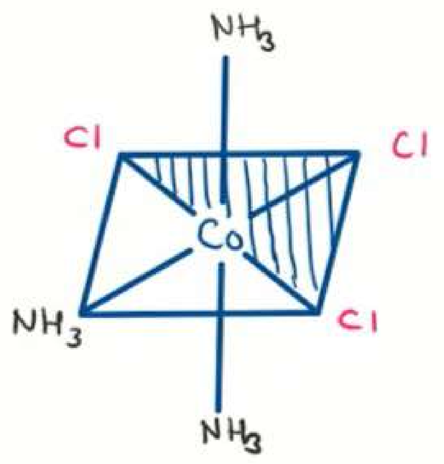


trans (mer) isomer

- **Example** :- $[Co(NH_3)_3Cl_3]$



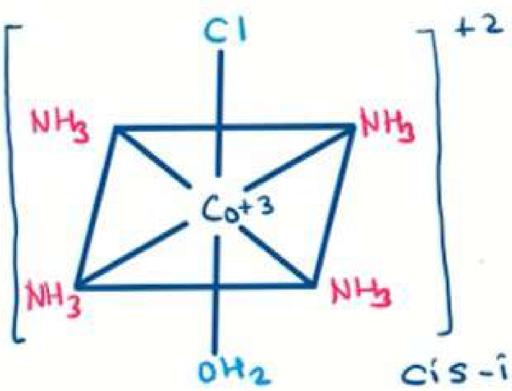
cis (fac) isomer



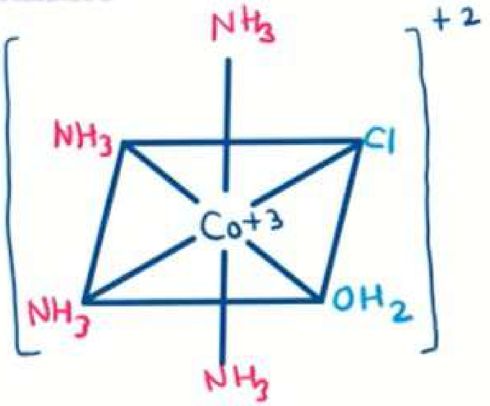
trans (mer) isomer

④ Octahedral complexes of $[Ma_4bc]$ type :→

- Example :- $[Co(NH_3)_4(H_2O)Cl]^{+2}$



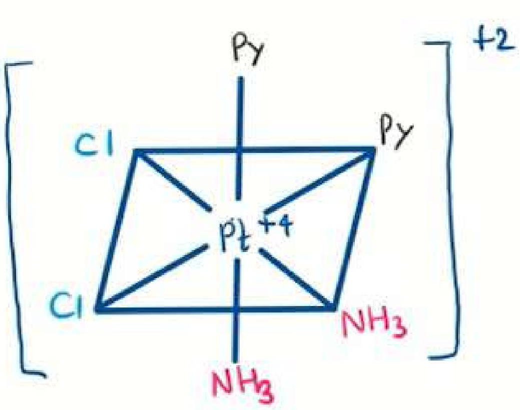
cis-isomer



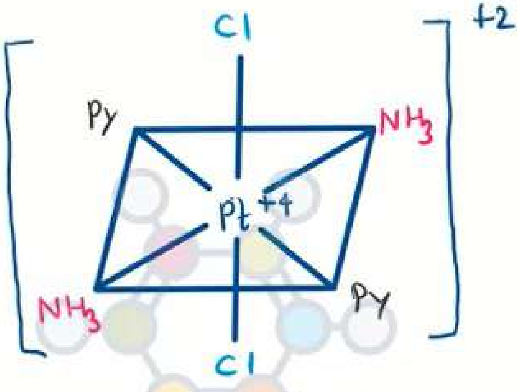
tran-isomer

⑤ Octahedral complexes of $[Ma_2b_2c_2]$ type:→

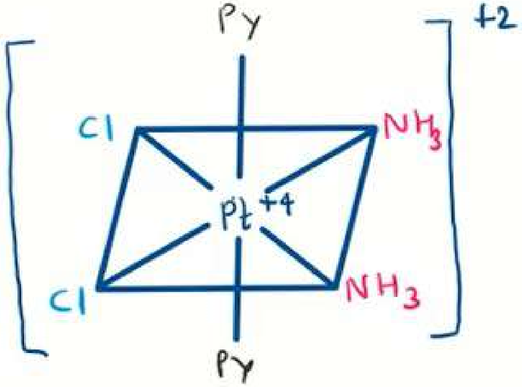
- **Example:-** $[Pt(NH_3)_2(Py)_2Cl_2]^{+2}$ has five isomers



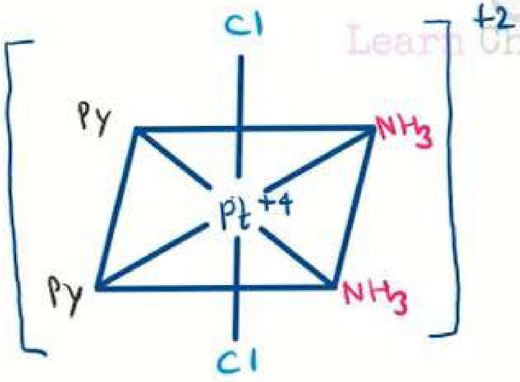
(i) cis



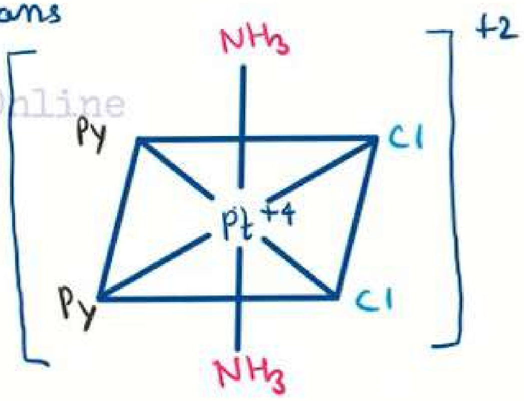
(ii) trans



(iii)



(iv)



(v)

⑥ octahedral complex of [Mabcdef] type:→

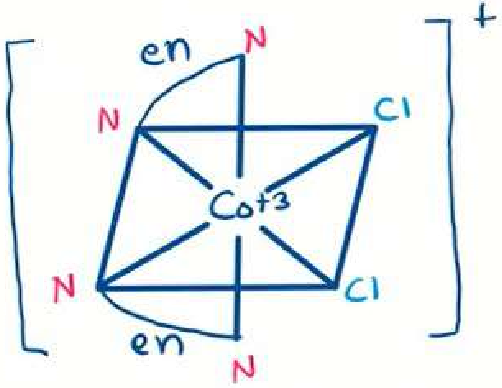
- This type of complex has 15 isomers but only three have been isolated.

⑦ Octahedral complex of $[M(AA)_3]$ type

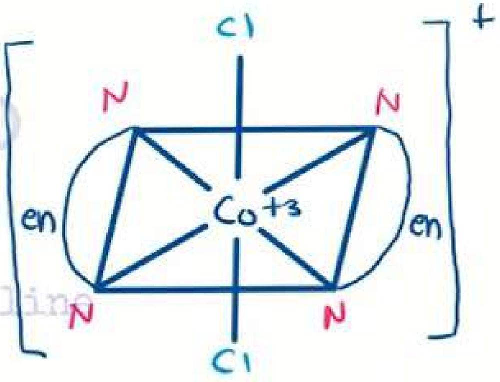
- does not show geometrical isomerism.

⑧ Octahedral complex of $[M(AA)_2a_2]$ type.

- <u>Example</u>:- $[Co(en)_2Cl_2]^+$



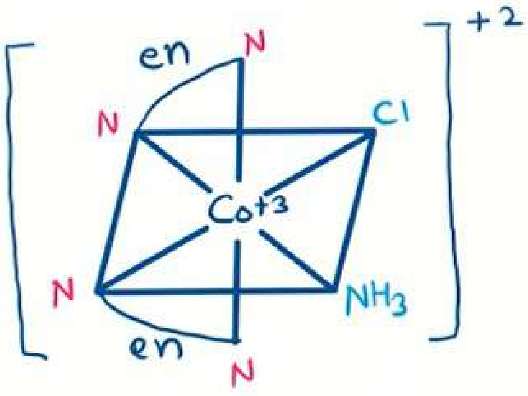
cis-isomer



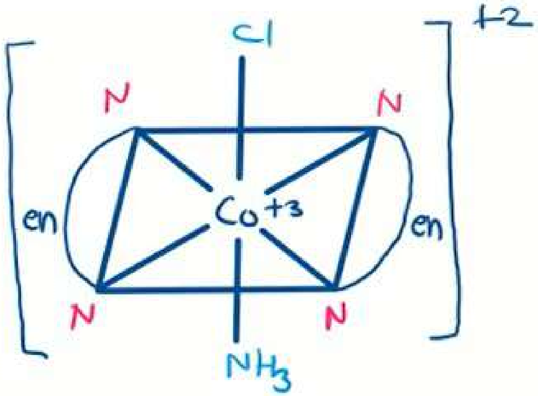
trans-isomer

⑨ octahedral complex of $[M(AA)_2ab]$ type

- Example $[Co(en)_2(NH_3)Cl]^{+2}$



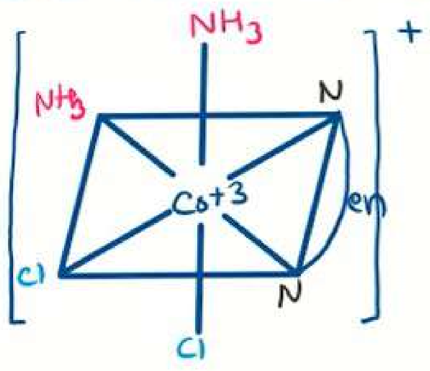
cis - isomer



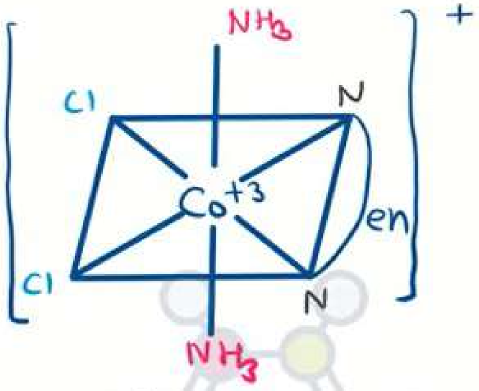
trans - isomer

⑩ octahedral complexes of $[M(AA)a_2b_2]$ type:→

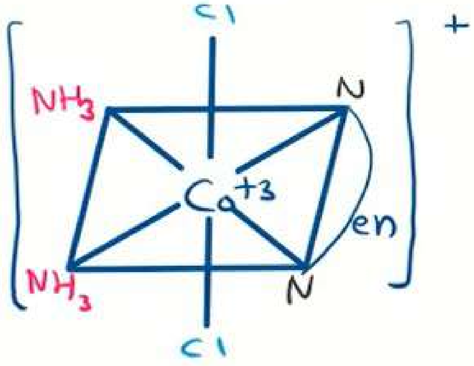
- **Example** :- $[Co(en)(NH_3)_2Cl_2]^+$



cis- isomer



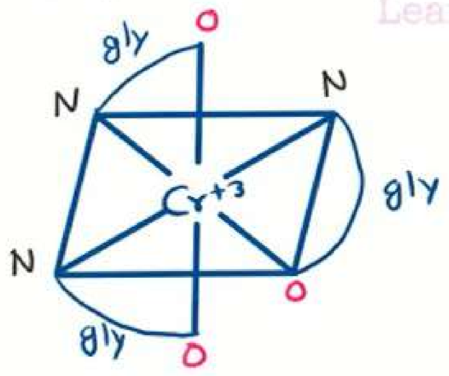
trans-isomer



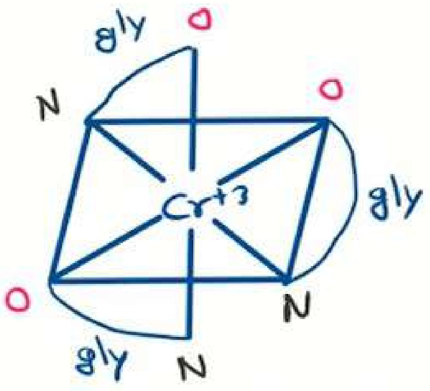
trans isomer

⑪ octahedral complexes of $[M(AB)_3]$ type.

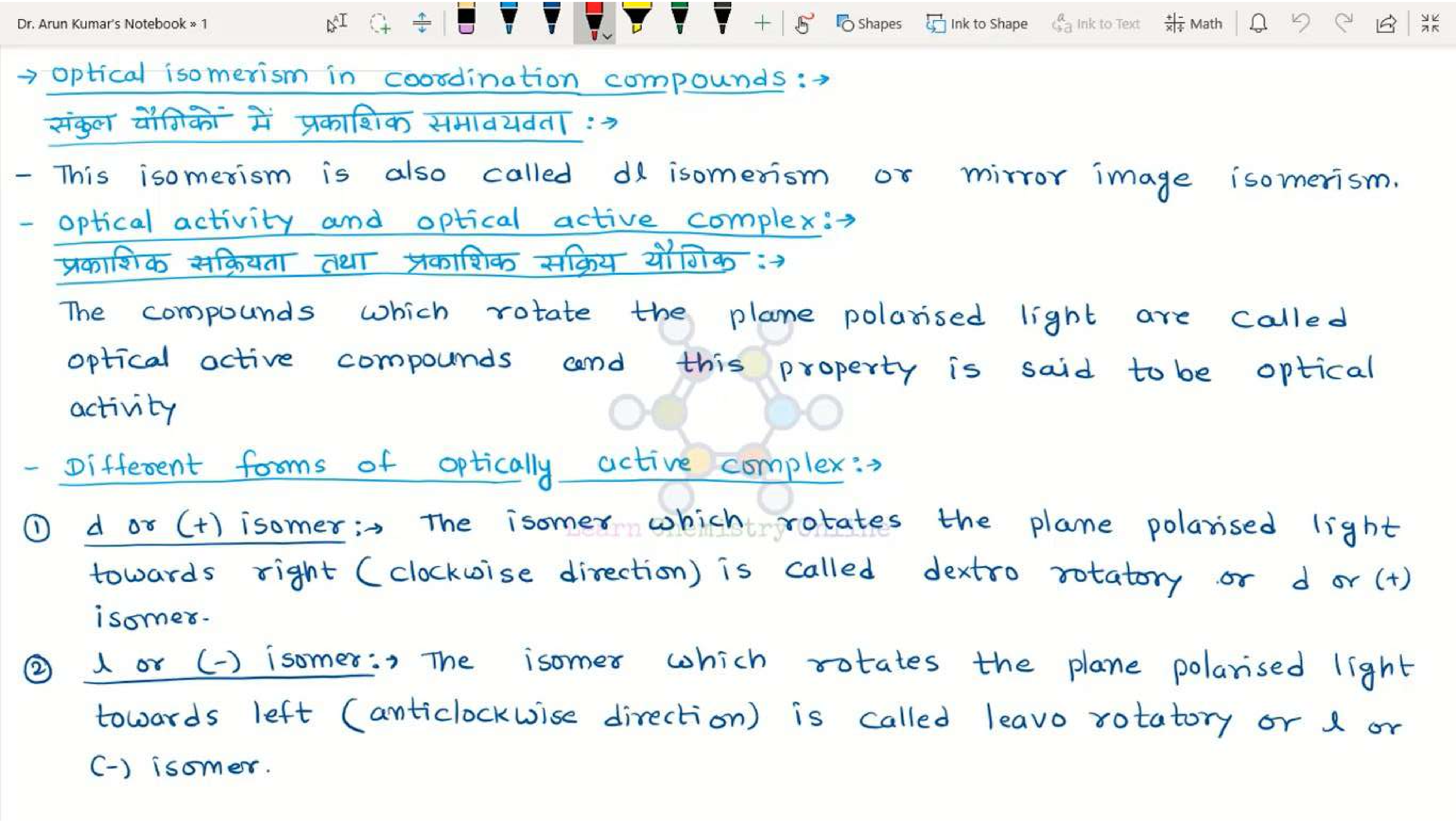
- **Example** :- $[Cr^{+3}(gly)_3]^0$



cis -isomer



trans -isomer



→ Optical isomerism in coordination compounds :→

संकुल यौगिकों में प्रकाशिक समावयवता :→

- This isomerism is also called dl isomerism or mirror image isomerism.
- Optical activity and optical active complex :→

प्रकाशिक सक्रियता तथा प्रकाशिक सक्रिय यौगिक :→

The compounds which rotate the plane polarised light are called optical active compounds and this property is said to be optical activity

- Different forms of optically active complex :→

① d or (+) isomer :→ The isomer which rotates the plane polarised light towards right (clockwise direction) is called dextro rotatory or d or (+) isomer.

② l or (-) isomer :→ The isomer which rotates the plane polarised light towards left (anticlockwise direction) is called leavo rotatory or l or (-) isomer.

③ optically inactive compounds :→

- The isomer which is not able to rotate the plane polarised light is called optically inactive compounds.

  example :- Racemic mixture, meso form etc.

→ Properties of d and l isomers :→

- d and l have same physical and chemical properties but they differ in their action on plane polarised light.
- d and l are mirror image of each other.
- These optical isomers also called mirror-image isomers or optical antipods or enantiomorphs or enantiomers.

→ Conditions for a molecule to show optical isomerism.

- molecule must be asymmetric. i.e. contains different groups of the atoms.
- molecule does not contains symmetry element (plane of symmetry, centre of symmetry and axis of symmetry.
- mirror image should not be superimposed on each other

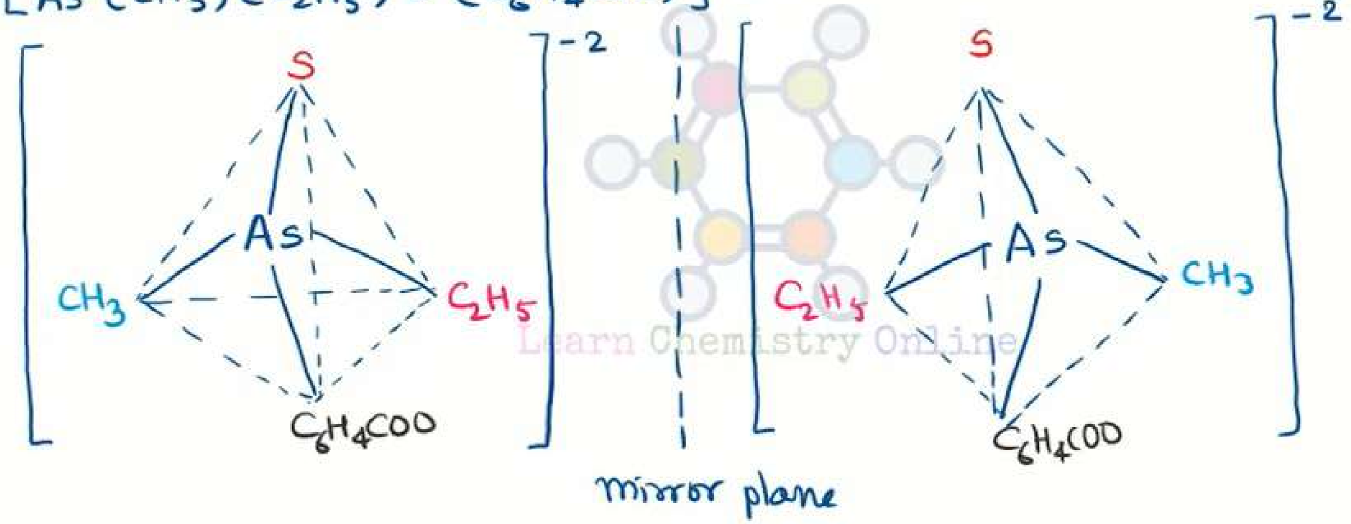
→ optical isomerism in Tetrahedral Complexes (C.N. - 4)

① Tetrahedral complexes of $[Ma_4]$, $[Ma_2b_2]$ and $[Ma_3b]$ type:-

- These complexes do not show optical isomerism because all the possible arrangements of ligands around the central metal atom are equivalent.

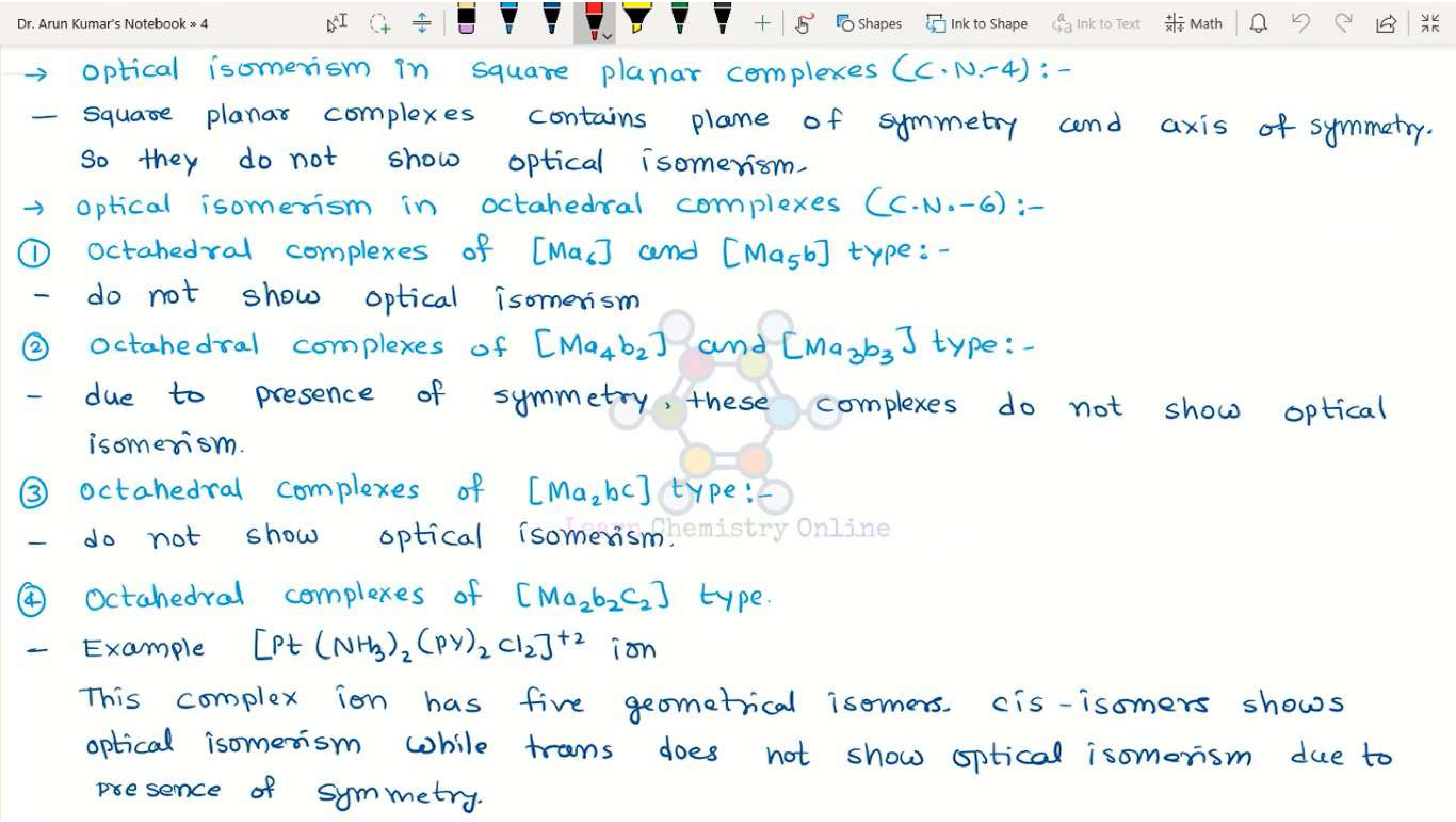
② Tetrahedral complexes of [Mabcd] type:-

- **Example** :- $[As(CH_3)(C_2H_5)S(C_6H_4COO)]^{-2}$



- Tetrahedral complexes of Be(II), B(III) and Zn(II) with symmetrical bidentate ligands also show optical isomerism.

example $[B(C_6H_4OCHO)_2]^+$, $[Be(C_6H_5CO.CH.CH_3CO)_2]^0$ etc.



→ optical isomerism in square planar complexes (C.N.-4) :-

— Square planar complexes contains plane of symmetry and axis of symmetry. So they do not show optical isomerism.

→ optical isomerism in octahedral complexes (C.N.-6) :-

① Octahedral complexes of $[Ma_6]$ and $[Ma_5b]$ type :-

- do not show optical isomerism

② Octahedral complexes of $[Ma_4b_2]$ and $[Ma_3b_3]$ type :-

- due to presence of symmetry, these complexes do not show optical isomerism.

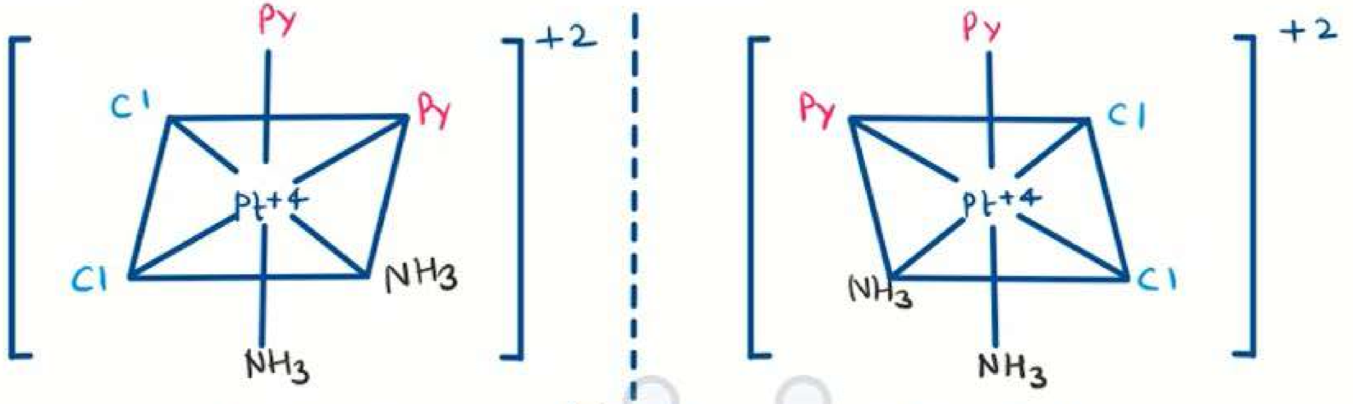
③ octahedral complexes of $[Ma_2bc]$ type :-

- do not show optical isomerism.

④ Octahedral complexes of $[Ma_2b_2c_2]$ type.

- Example $[Pt(NH_3)_2(py)_2Cl_2]^{+2}$ ion

This complex ion has five geometrical isomers. cis-isomers shows optical isomerism while trans does not show optical isomerism due to presence of symmetry.

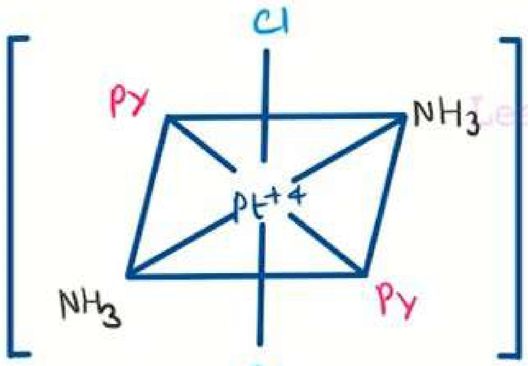


cis - d - isomer

Mirror plane

cis - l - isomer

mirror image of cis $[Pt(NH_3)_2(PY)_2Cl_2]^{+2}$ ion

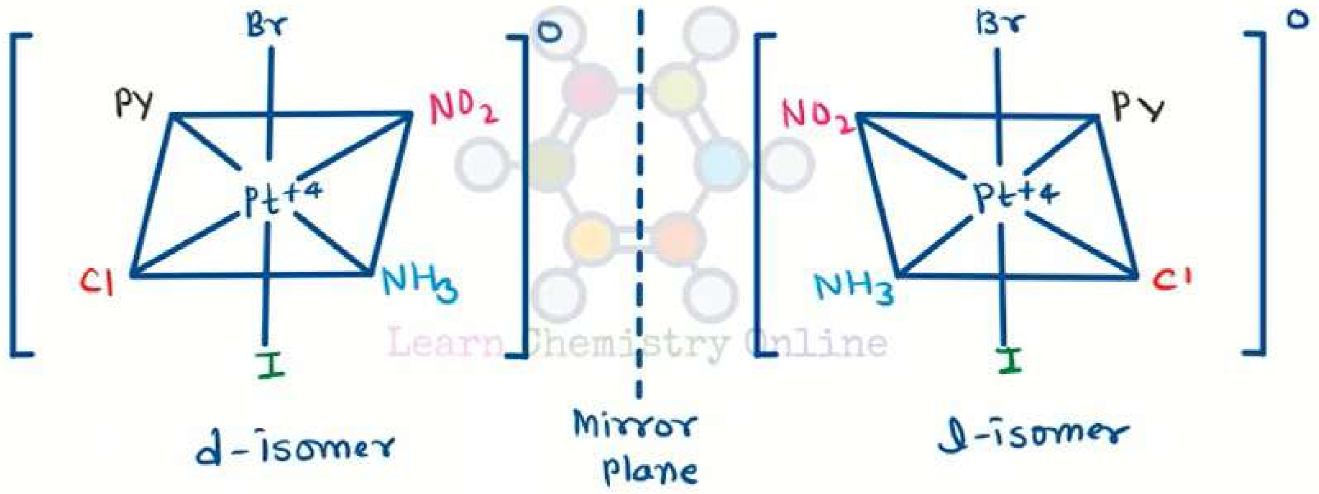


trans isomer

trans $[Pt(NH_3)_2(PY)_2Cl_2]^{+2}$ ion does not show optical isomer

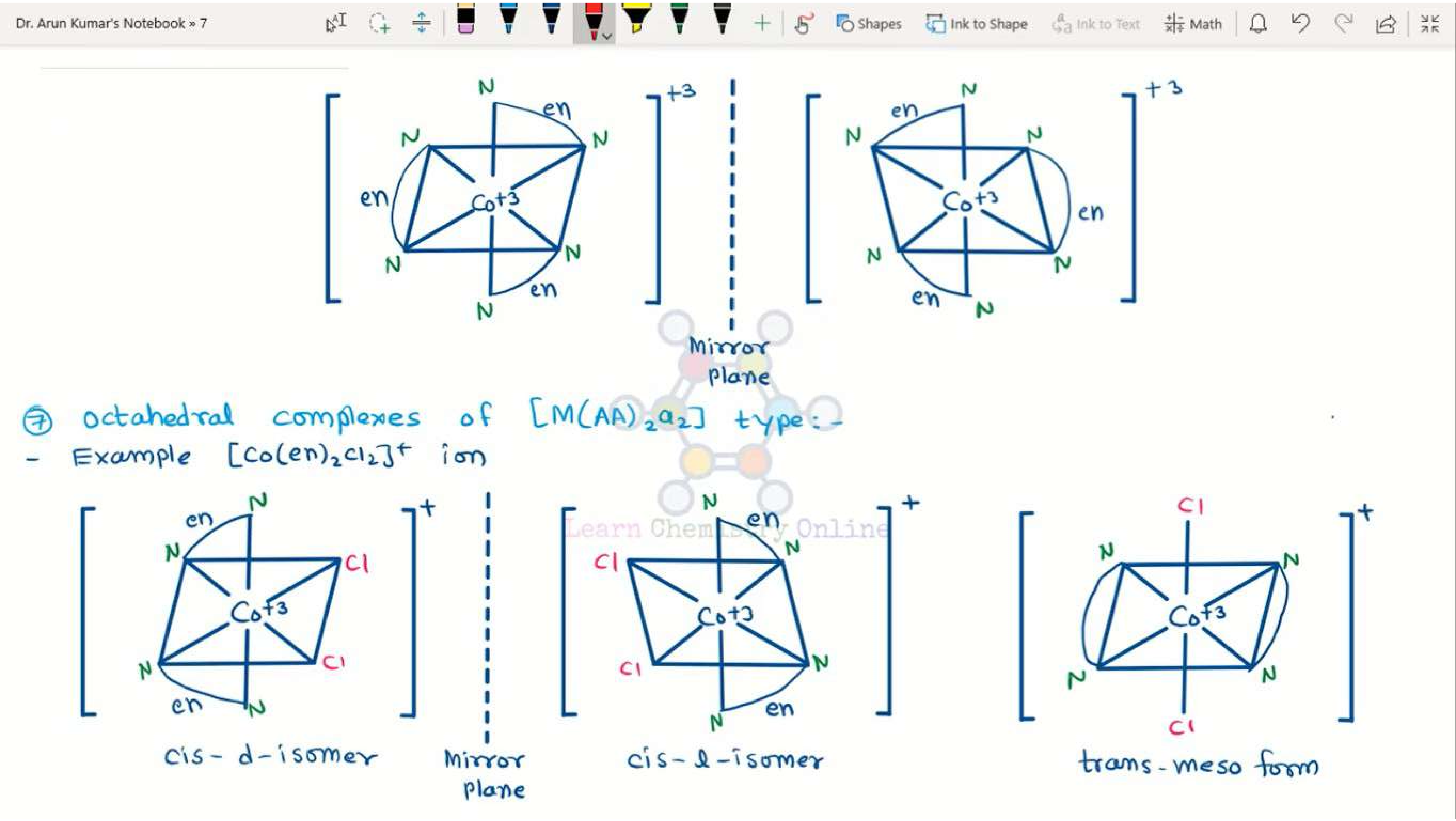
⑤ octahedral complex of [Mabcdef] type :-

- This complex has 15 geometrical isomers. all 15 isomers shows optical isomerism and give total 30 optical isomers (15 d + 15 l isomers)
- example of one isomer of $[Pt(NH_3)BrClI(NO_2)(py)]^0$



⑥ octahedral complex of $[M(AA)_3]$ type :→

- Example $[Co(en)_3]^{+3}$ ion



⑦ octahedral complexes of $[M(AA)_2a_2]$ type:-

- Example $[Co(en)_2Cl_2]^+$ ion

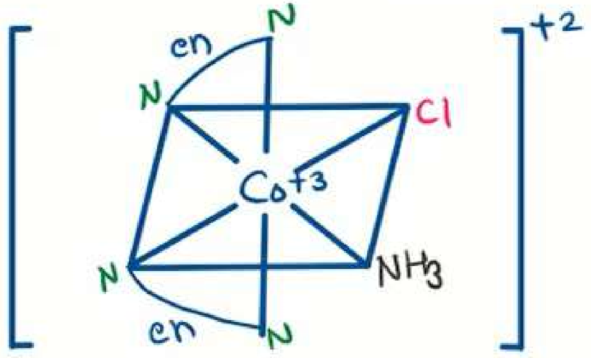
cis-d-isomer

cis-l-isomer

trans-meso form

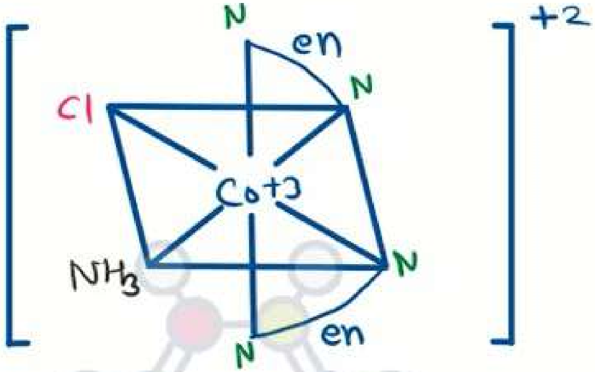
⑧ octahedral complexes of $[M(AA)_2ab]$ type :-

- Example $[Co(en)_2(NH_3)Cl]^{+2}$

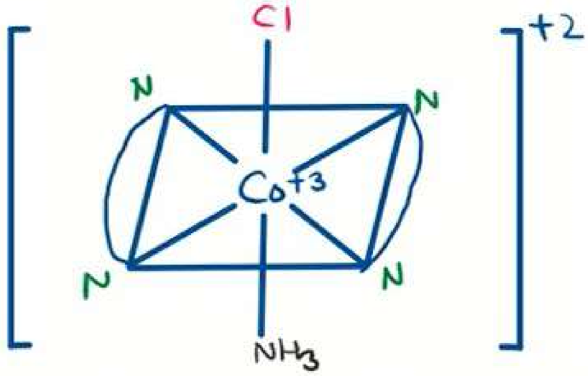


cis - d - isomer

plane



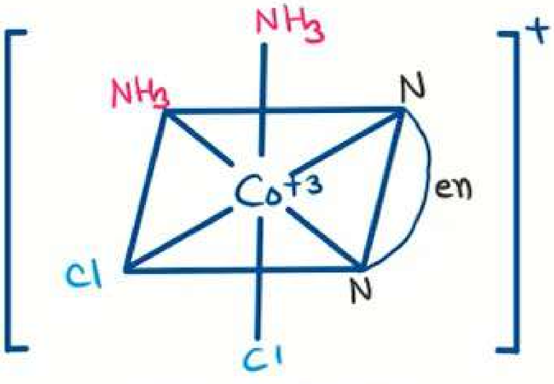
cis - l - isomer



trans - meso form

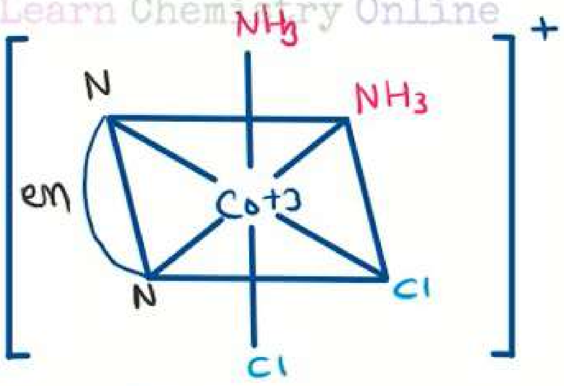
⑨ octahedral complexes of $[M(AA)a_2b_2]$ type :-

- Example $[Co(en)(NH_3)_2Cl_2]^+$ ion

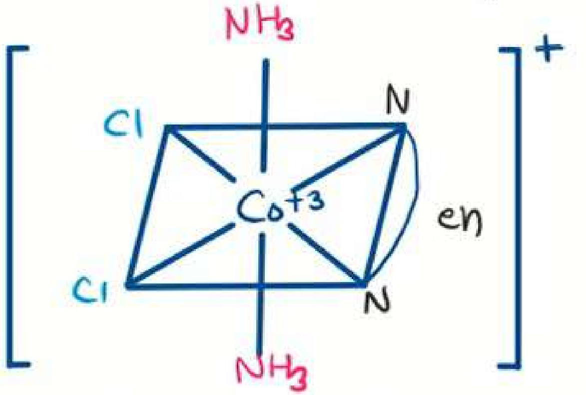


cis - d - isomer

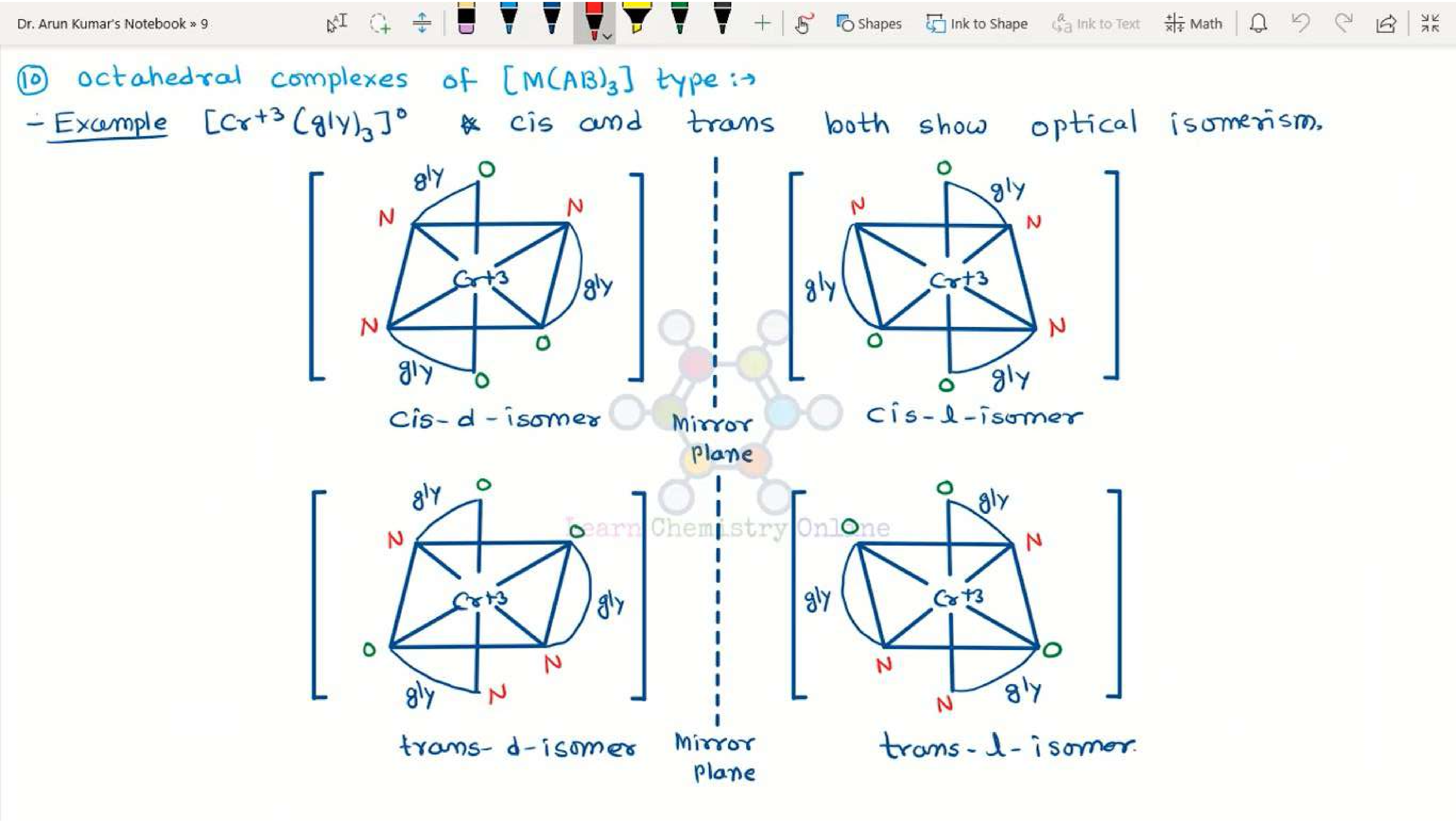
plane



cis - l - isomer



trans - meso form



⑩ octahedral complexes of $[M(AB)_3]$ type :→

- Example $[Cr^{+3}(gly)_3]^0$ ✱ cis and trans both show optical isomerism.

Cis-d-isomer

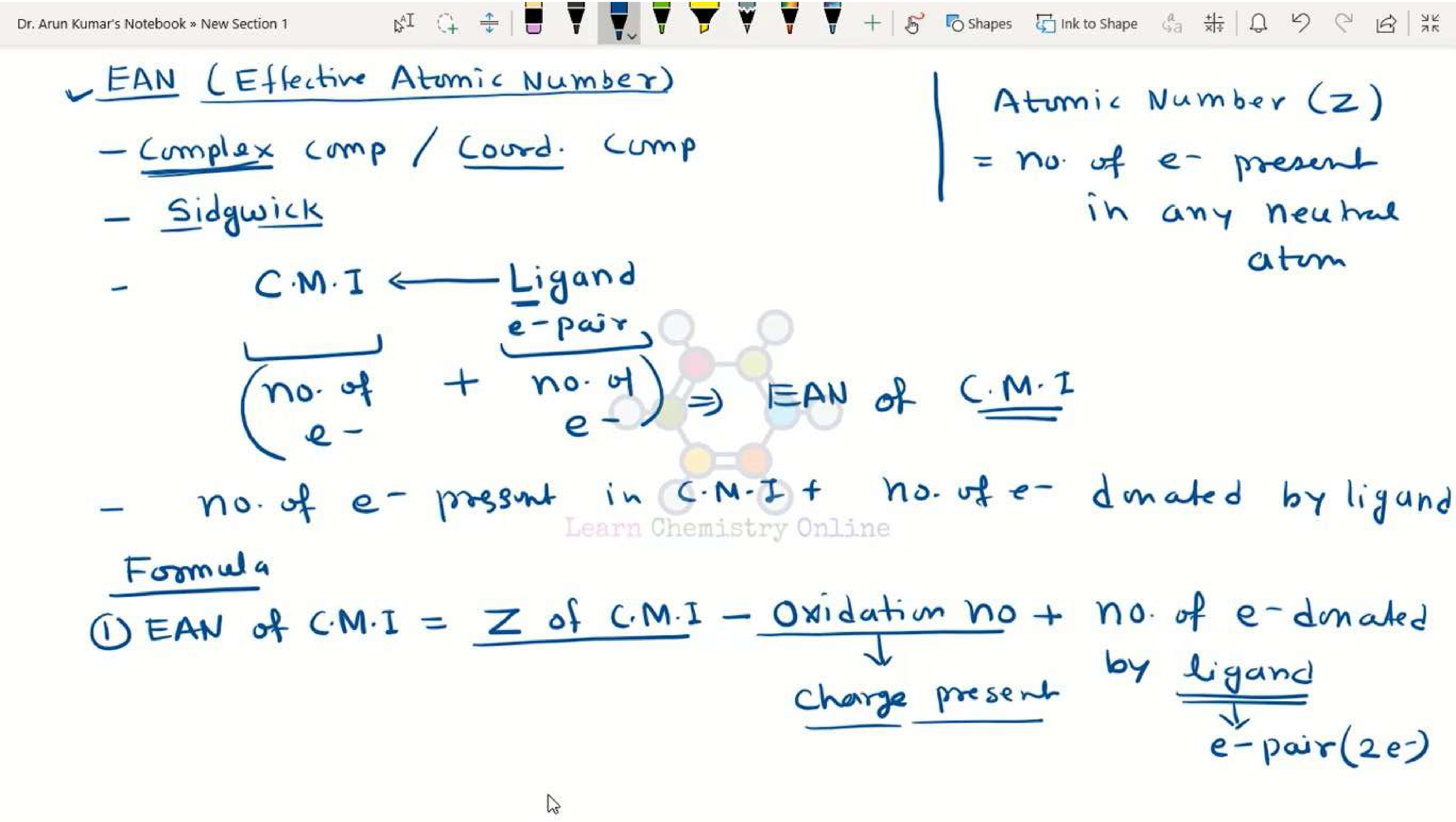
Mirror plane

Cis-l-isomer

trans-d-isomer

Mirror plane

trans-l-isomer.



✓ **EAN (Effective Atomic Number)**

- Complex comp / Coord. comp
- Sidgwick
- $$\underbrace{\text{C.M.I}}_{} \longleftarrow \underbrace{\underline{\text{L}}\text{igand}}_{\text{e-pair}}$$

$$\left(\begin{matrix}\text{no. of} \\ \text{e}^-\end{matrix} + \begin{matrix}\text{no. of} \\ \text{e}^-\end{matrix}\right) \Rightarrow \text{EAN of } \underline{\underline{\text{C.M.I}}}$$

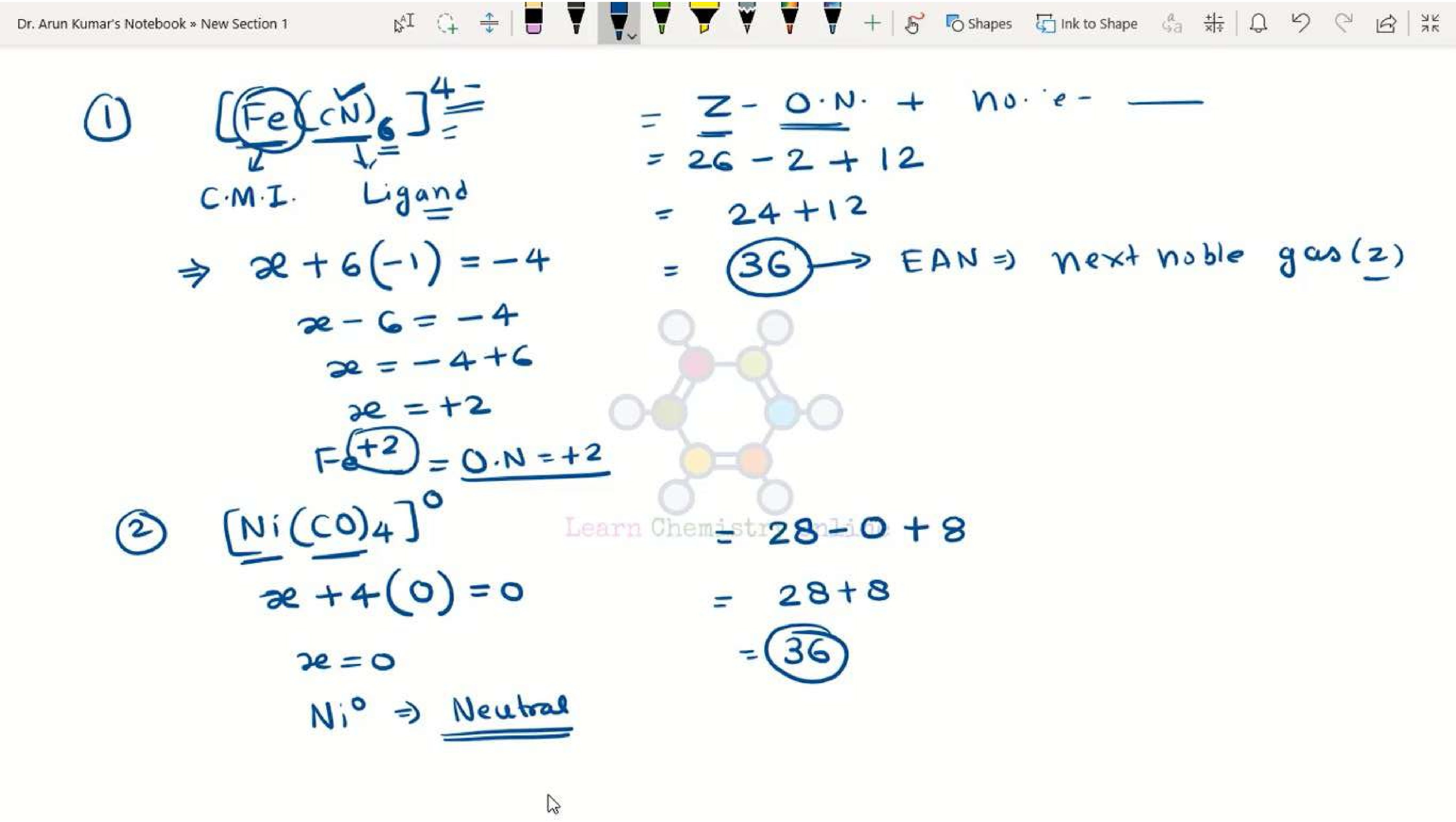
- no. of e⁻ present in C.M.I + no. of e⁻ donated by ligand

Atomic Number (Z)

= no. of e⁻ present in any neutral atom

Formula

① $$\text{EAN of C.M.I} = \underline{\text{Z of C.M.I}} - \underbrace{\underline{\text{Oxidation no}}}_{\downarrow \; \underline{\text{Charge present}}} + \text{no. of e}^-\text{donated by } \underbrace{\underline{\underline{\text{ligand}}}}_{\downarrow \; \text{e-pair}(2\text{e}^-)}$$



① $[\boxed{Fe}(\underline{CN})_6]^{4-}$

C.M.I. Ligand

$\Rightarrow x + 6(-1) = -4$

$x - 6 = -4$

$x = -4 + 6$

$x = +2$

$Fe^{\boxed{+2}} = \underline{O.N = +2}$

$= \underline{Z} - \underline{O.N.} + no.\ e^- \_\_\_\_$

$= 26 - 2 + 12$

$= 24 + 12$

$= \boxed{36} \longrightarrow$ EAN ⇒ next noble gas (z)

② $[\underline{Ni}(\underline{CO})_4]^0$

$x + 4(0) = 0$

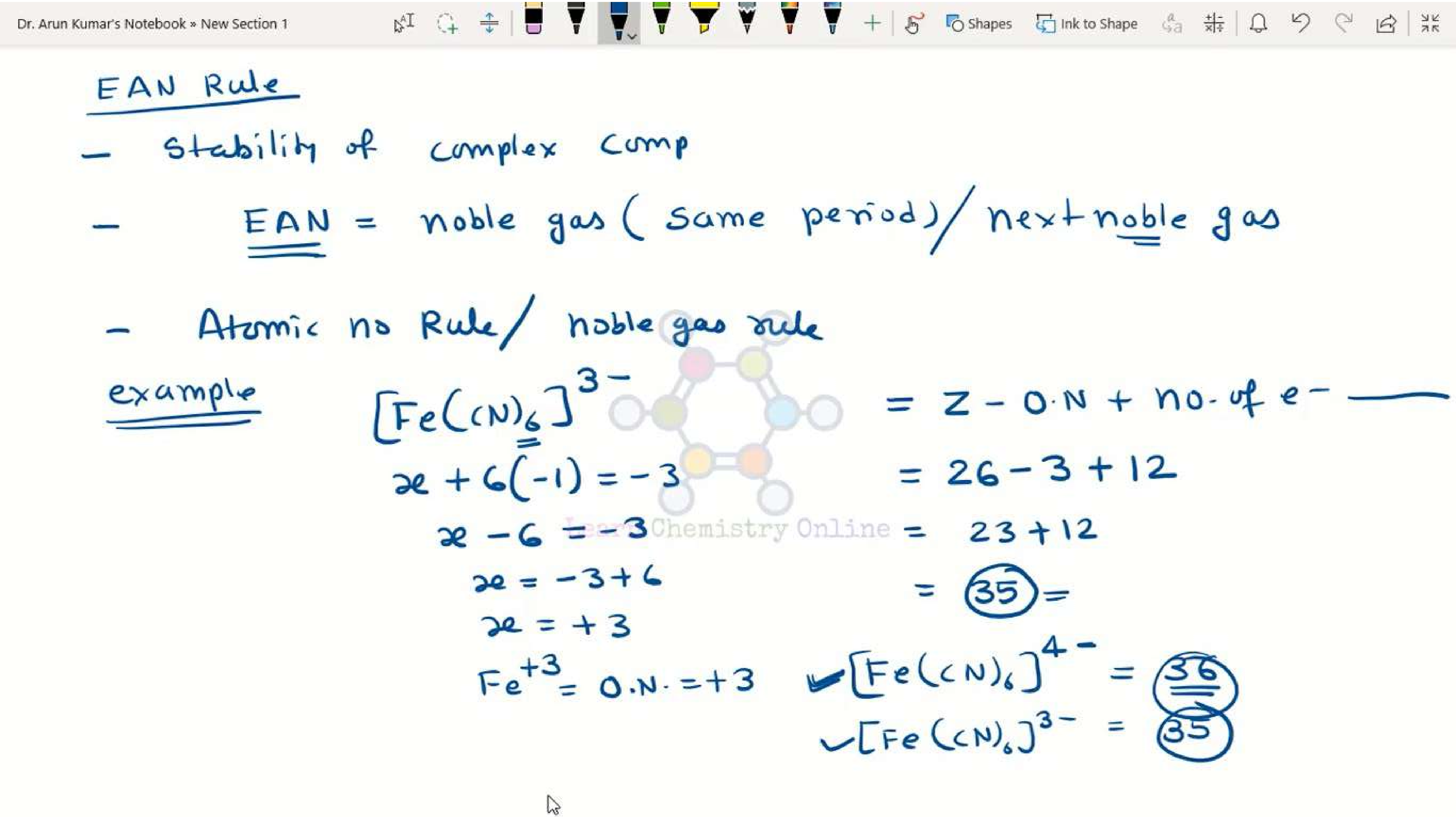
$x = 0$

$Ni^0 \Rightarrow \underline{Neutral}$

$= 28 - 0 + 8$

$= 28 + 8$

$= \boxed{36}$



EAN Rule

- Stability of complex comp
- $\underline{\underline{\text{EAN}}}$ = noble gas (same period)/ next $\underline{\underline{\text{no}}}$ble gas
- Atomic no Rule/ noble gas rule

$\underline{\underline{\text{example}}}$

$[Fe(CN)_{\underline{\underline{6}}}]^{3-}$ $= Z - O.N + \text{no. of } e^- \text{———}$

$x + 6(-1) = -3$ $= 26 - 3 + 12$

$x - 6 = -3$ $= 23 + 12$

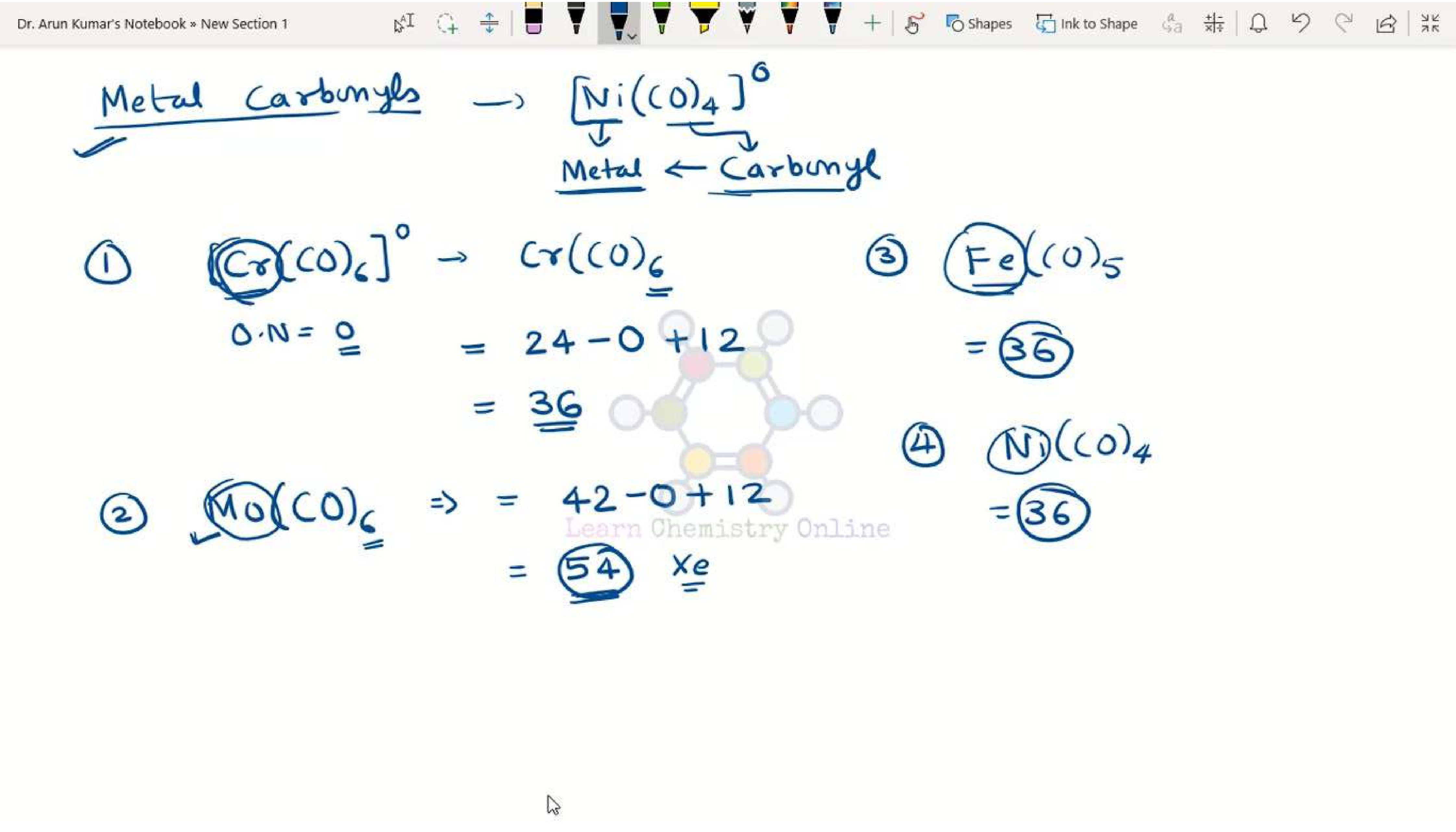
$x = -3 + 6$ $= \boxed{35} =$

$x = +3$

$Fe^{+3} = O.N. = +3$

✓ $[Fe(CN)_6]^{4-} = \boxed{\underline{\underline{36}}}$

✓ $[Fe(CN)_6]^{3-} = \boxed{35}$



Metal Carbonyls → $[Ni(CO)_4]^0$

Metal ← Carbonyl

① $[Cr(CO)_6]^0 \rightarrow Cr(CO)_6$

O.N = 0

$= 24 - 0 + 12$

$= 36$

② $Mo(CO)_6 \Rightarrow = 42 - 0 + 12$

$= 54$ Xe

③ $Fe(CO)_5$

$= 36$

④ $Ni(CO)_4$

$= 36$

Polynuclear metal carbonyls

many Metal

$Co_2(CO)_8$ = $27 \times 2 = 54$

$2 \times 8 = 16$

One Co-Co = 2 (2 e- in one bond)

$\overline{72}$

$= \frac{72}{2} \Rightarrow \boxed{36}$

$Fe_3(CO)_{12}$ = $26 \times 3 = 78$

$2 \times 12 = 24$

Three Fe-Fe b = 6

$\overline{108}$

$= \frac{108}{3} = \boxed{36}$

✯ EAN = Metal carbonyl → no. of metal-metal bond

$Co_2(CO)_8$ = 54 (27×2)

= 16 (8×2)

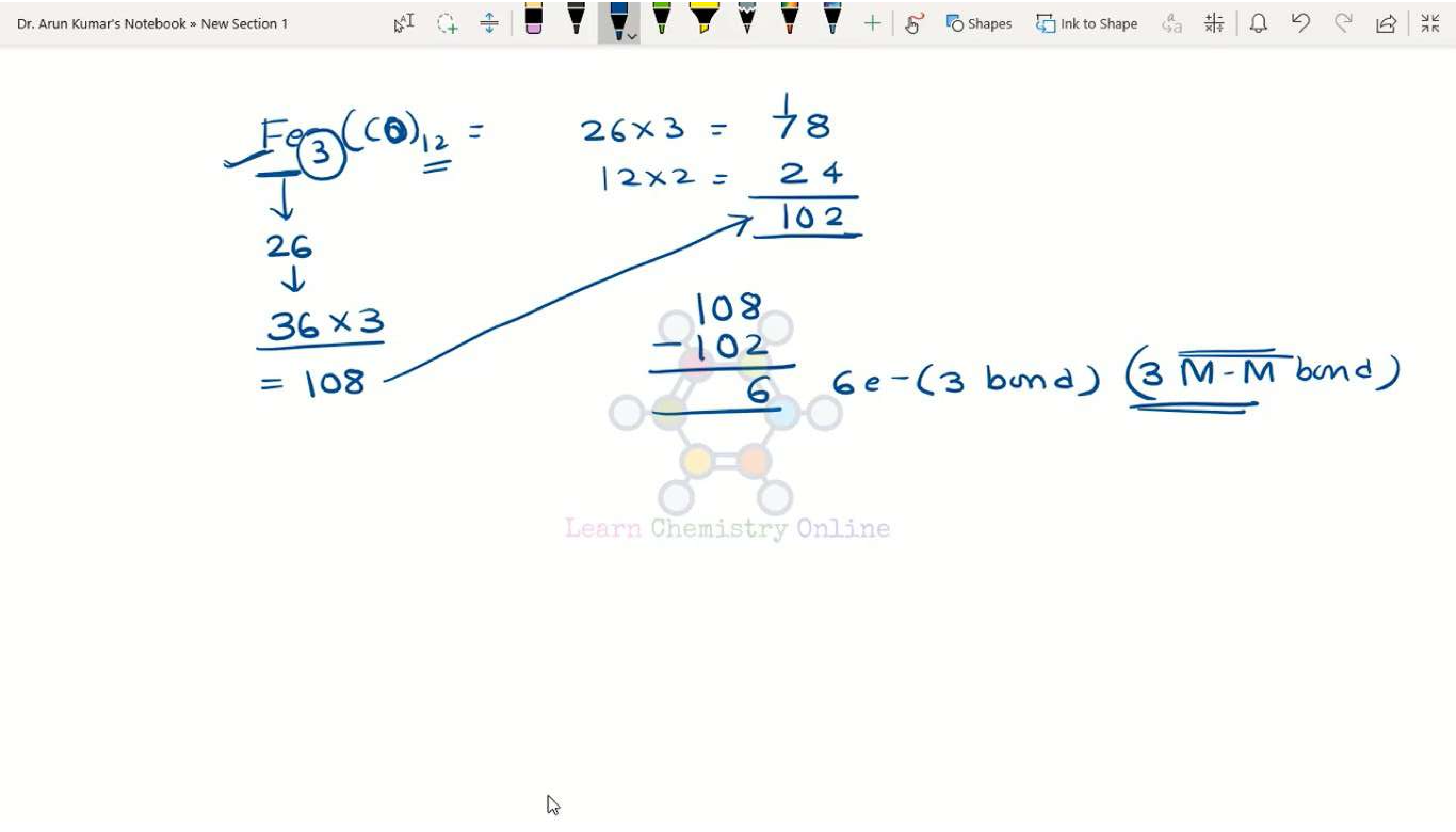
70

36×2

72

$$\begin{array}{r} 72 \\ -70 \\ \hline 2 \end{array}$$

2e⁻ (1 metal-metal)



$Fe_{\textcircled{3}}(CO)_{12}$ =

Fe ↓ 26 ↓ 36 × 3

= 108

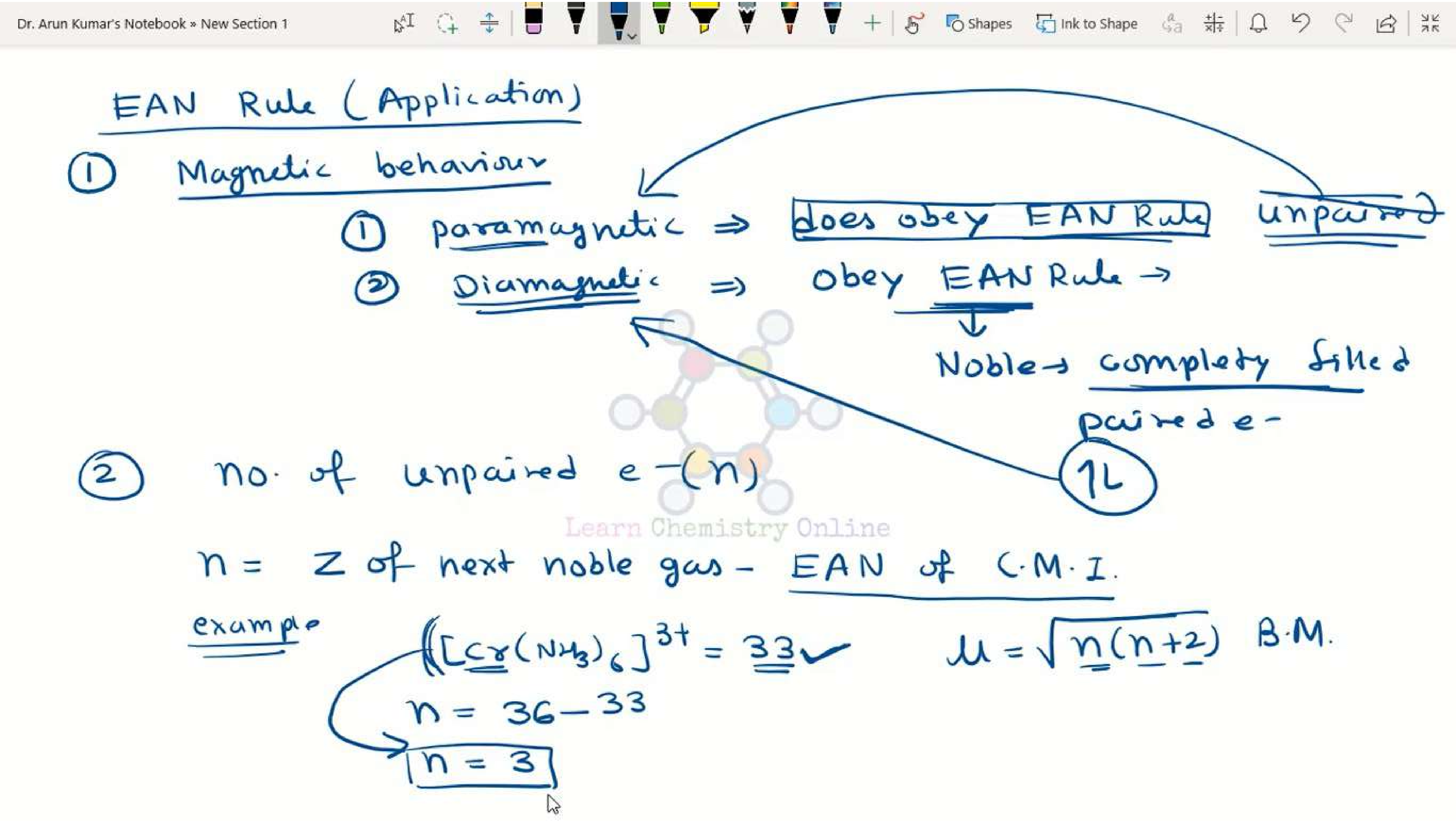
26 × 3 = 78

12 × 2 = 24

102

$$\begin{array}{r} 108 \\ -102 \\ \hline 6 \end{array}$$

6e⁻ (3 bond) (3 M-M bond)



EAN Rule (Application)

① Magnetic behaviour

① paramagnetic ⇒ $\boxed{\text{does obey EAN Rule}}$ unpaired

② Diamagnetic ⇒ obey EAN Rule →

↓

Noble → completely filled paired e-

1L

② no. of unpaired e⁻ (n)

n = Z of next noble gas − EAN of C.M.I.

example

$[Cr(NH_3)_6]^{3+} = 33$ ✓

$n = 36 - 33$

$\boxed{n = 3}$

$\mu = \sqrt{n(n+2)}$ B.M.

③ <u>stability of complex</u>

Obey EAN Rule = more stable

does not EAN Rule = less stable

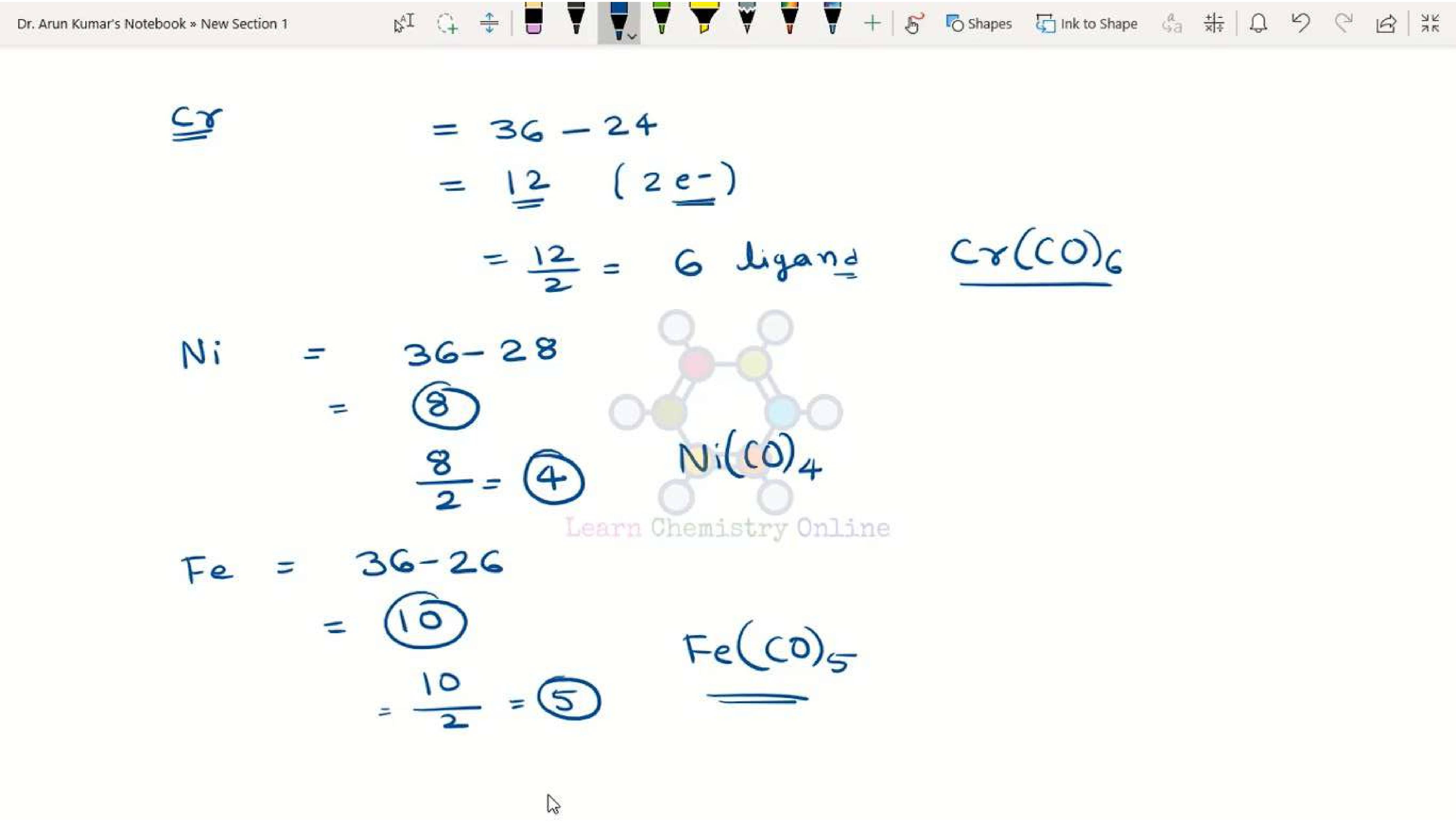
✓ $[Fe(CN)_6]^{4-}$ ✓ $[Fe(CN)_6]^{3-}$

36 ㉟

④ no. of ligands attached with C.M.I in Carbonyl compounds

✓ Fe, Cr, Ni

No. of CO ligands = 36 − Z of C.M.I.



$\underline{\underline{Cr}}$ $= 36 - 24$

$= \underline{\underline{12}} \quad (2\underline{\underline{e^-}})$

$= \frac{12}{2} = 6$ ligan$\underline{\underline{d}}$ $\quad \underline{Cr(CO)_6}$

$Ni = 36 - 28$

$= \textcircled{8}$

$\frac{8}{2} = \textcircled{4} \quad Ni(CO)_4$

$Fe = 36 - 26$

$= \textcircled{10}$

$= \frac{10}{2} = \textcircled{5} \quad \underline{\underline{Fe(CO)_5}}$

Valence bond theory

- Pauling - 1930

Main point

① ligand donates e⁻ pair to metal ion

$$\underset{\text{donor}}{\underline{L}} \longrightarrow \underset{\text{Acceptor}}{\underline{M}}$$

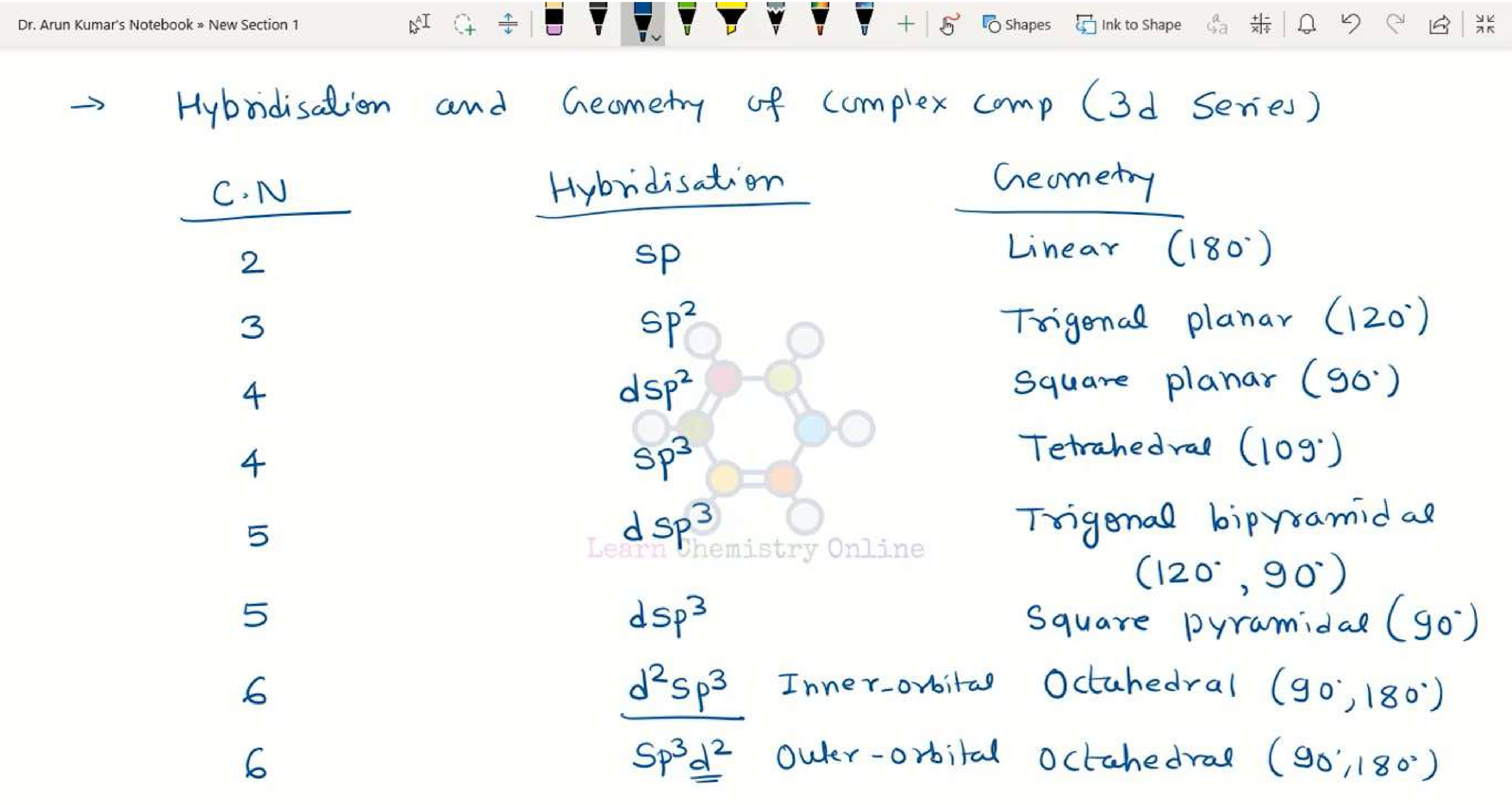
② Metal ion must have Vacant hybrid orbitals

③ Vacant hybrids orbitals must have equal in energy and geometry

④ no. of Vacant hybrid orbitals = no. of coordinate bond

④ ⇒ C.N = ④

↓ coordination of C.M.I



→ Hybridisation and Geometry of Complex comp (3d Series)

C.N	Hybridisation		Geometry
2	sp		Linear (180°)
3	sp^2		Trigonal planar (120°)
4	dsp^2		Square planar (90°)
4	sp^3		Tetrahedral (109°)
5	dsp^3		Trigonal bipyramidal (120°, 90°)
5	dsp^3		Square pyramidal (90°)
6	$\underline{d^2sp^3}$	Inner-orbital	Octahedral (90°, 180°)
6	$sp^3\underline{\underline{d}}^2$	Outer-orbital	Octahedral (90°, 180°)

⇒ Octahedral complexes (C.N. = 6)

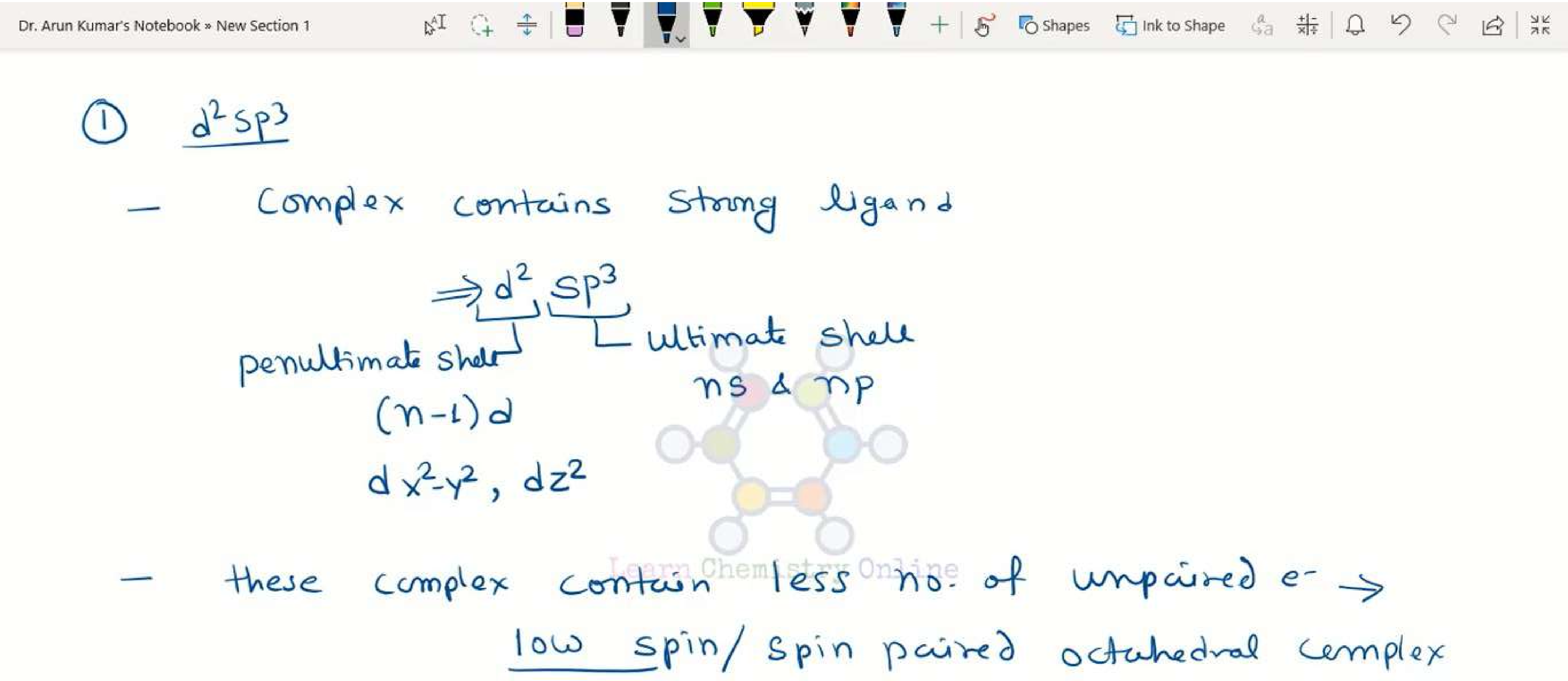
d^2sp^3, sp^3d] — Octahedral hybridisation

d^2sp^3 → Inner-orbital octahedral complex

sp^3d^2 → Outer- " " "

type of ligand →

ligand ↓ weak / strong



① $\underline{d^2sp^3}$

- Complex contains strong ligand

$$\Rightarrow \underbrace{d^2}_{\text{penultimate shell}} \underbrace{sp^3}_{\text{ultimate shell}}$$

penultimate shell

$(n-1)d$

$d_{x^2-y^2}$, d_{z^2}

ultimate shell

ns & np

- these complex contain less no. of unpaired e⁻ →

low spin/ spin paired octahedral complex

example

$[Fe(CN)_6]^{3-}$

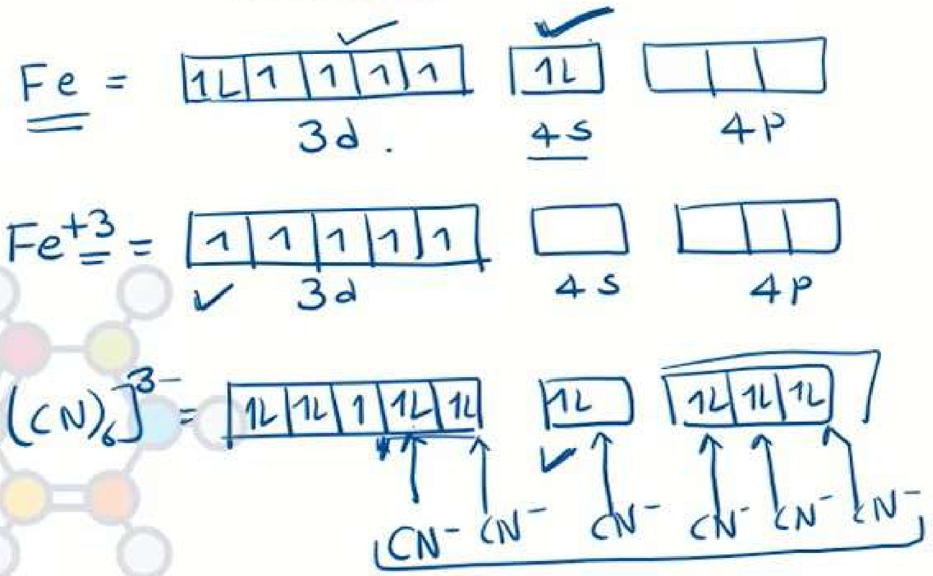
$x + 6(-1) = -3$

$x = 6 - 3$

$x = +3$

Fe^{+3}

$Fe = 3d^6\ 4s^2$



d^2sp^3

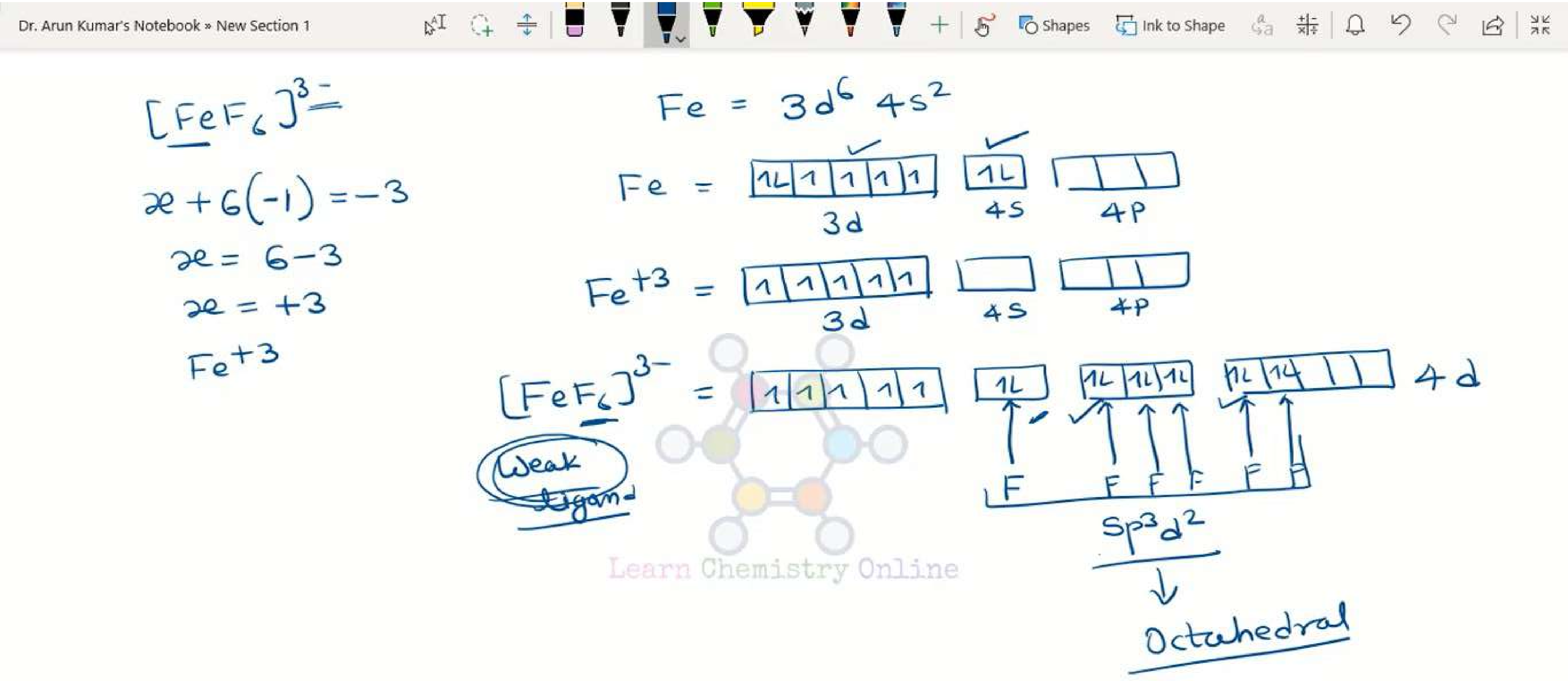
Octrahedral

② $\underline{sp^3d^2}$

→ Complex contains <u>weak ligand</u>

sp^3d^2
↓ outer shell
ns np $\underline{nd}$ └ $d_{x^2-y^2}$, d_{z^2}

→ greater no. of unpaired e⁻ → high spin/spin free octahedral complexes



$[FeF_6]^{3-}$

$x + 6(-1) = -3$

$x = 6 - 3$

$x = +3$

Fe^{+3}

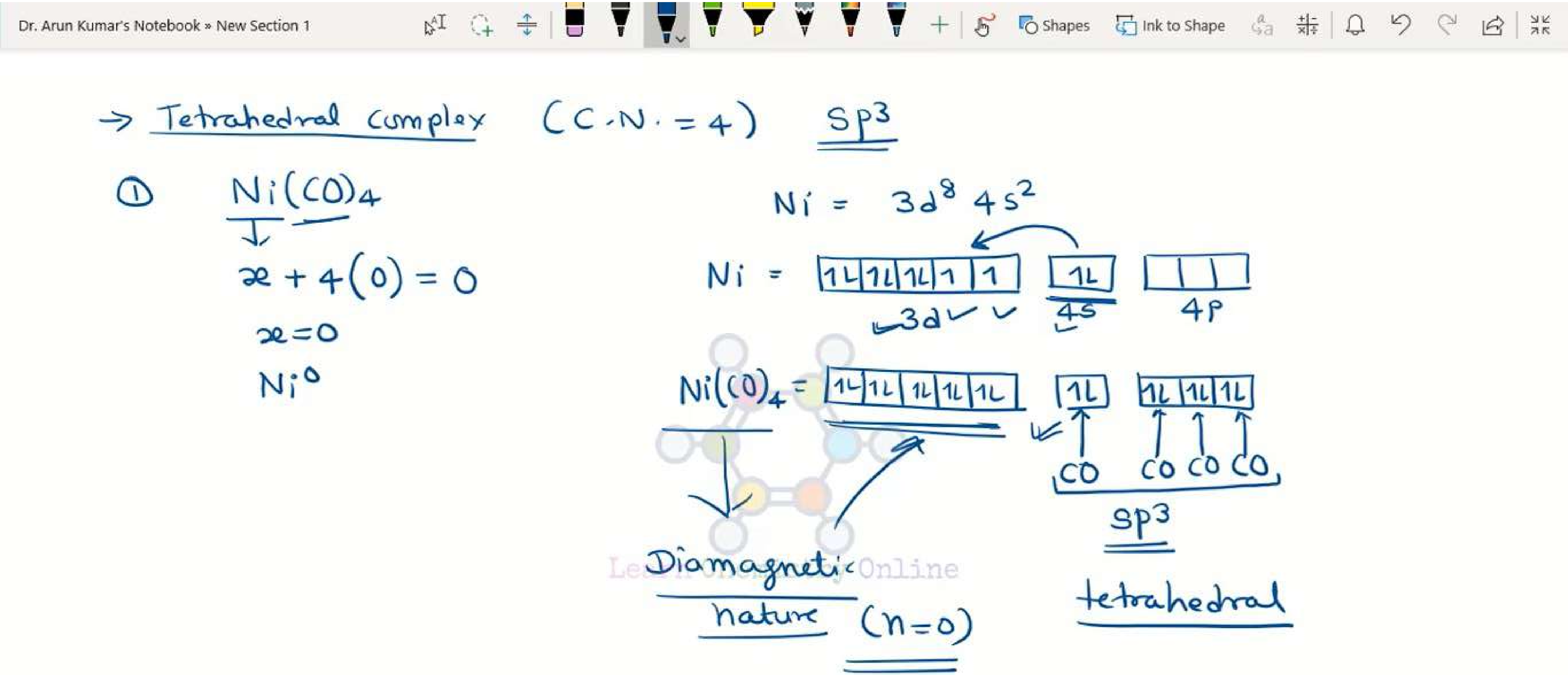
$Fe = 3d^6 4s^2$

Weak ligand

sp^3d^2

↓

Octahedral



→ Tetrahedral complex (C.N. = 4) sp^3

① $Ni(CO)_4$

$x + 4(0) = 0$

$x = 0$

Ni^0

$Ni = 3d^8\,4s^2$

Ni = | ↑↓ | ↑↓ | ↑↓ | ↑ | ↑ | | ↑↓ | | | | |
3d 4s 4p

$Ni(CO)_4$ = | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | | ↑↓ | | ↑↓ | ↑↓ | ↑↓ |

CO CO CO CO

sp^3

tetrahedral

Diamagnetic nature $(n=0)$

② $[\underline{Ni}Cl_4]^{2-}$

$x + 4(-1) = -2$

$x = 4 - 2$

$x = +2$

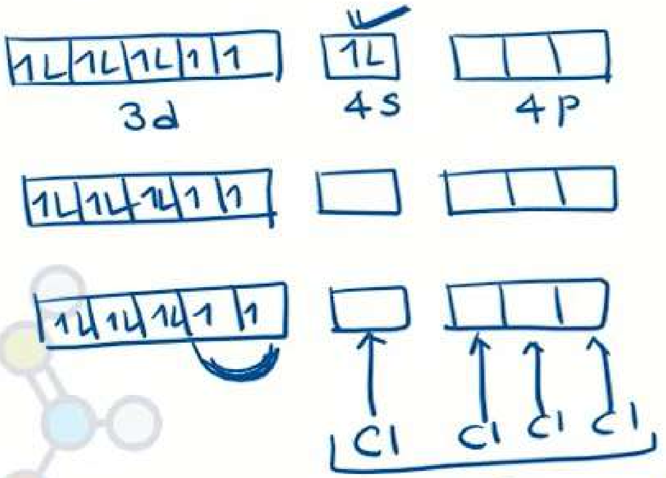
Ni^{+2}

$Ni = 3d^8 4s^2$

$Ni =$

$Ni^{+2} =$

$[NiCl_4]^{2-} =$



weak ligand
↓
unpaired

$\underline{\underline{sp^3}}$ → tetrahedral

→ **Square planar complex**

C.N = 4 dsp^2

$C.N. = 4 \begin{cases} sp^3 \rightarrow n = 2 \rightarrow \text{paramg} \\ \boxed{dsp^2} \rightarrow \boxed{n = 0} \rightarrow \boxed{\text{diamag}} \end{cases}$

① $[Ni(CN)_4]^{2-}$

$\downarrow$

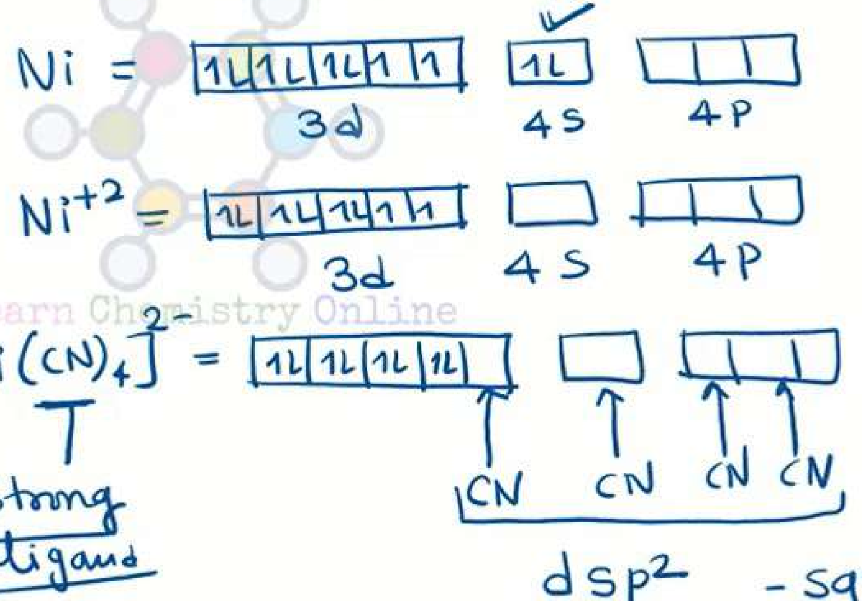
$x + 4(-1) = -2$

$x = 4 - 2$

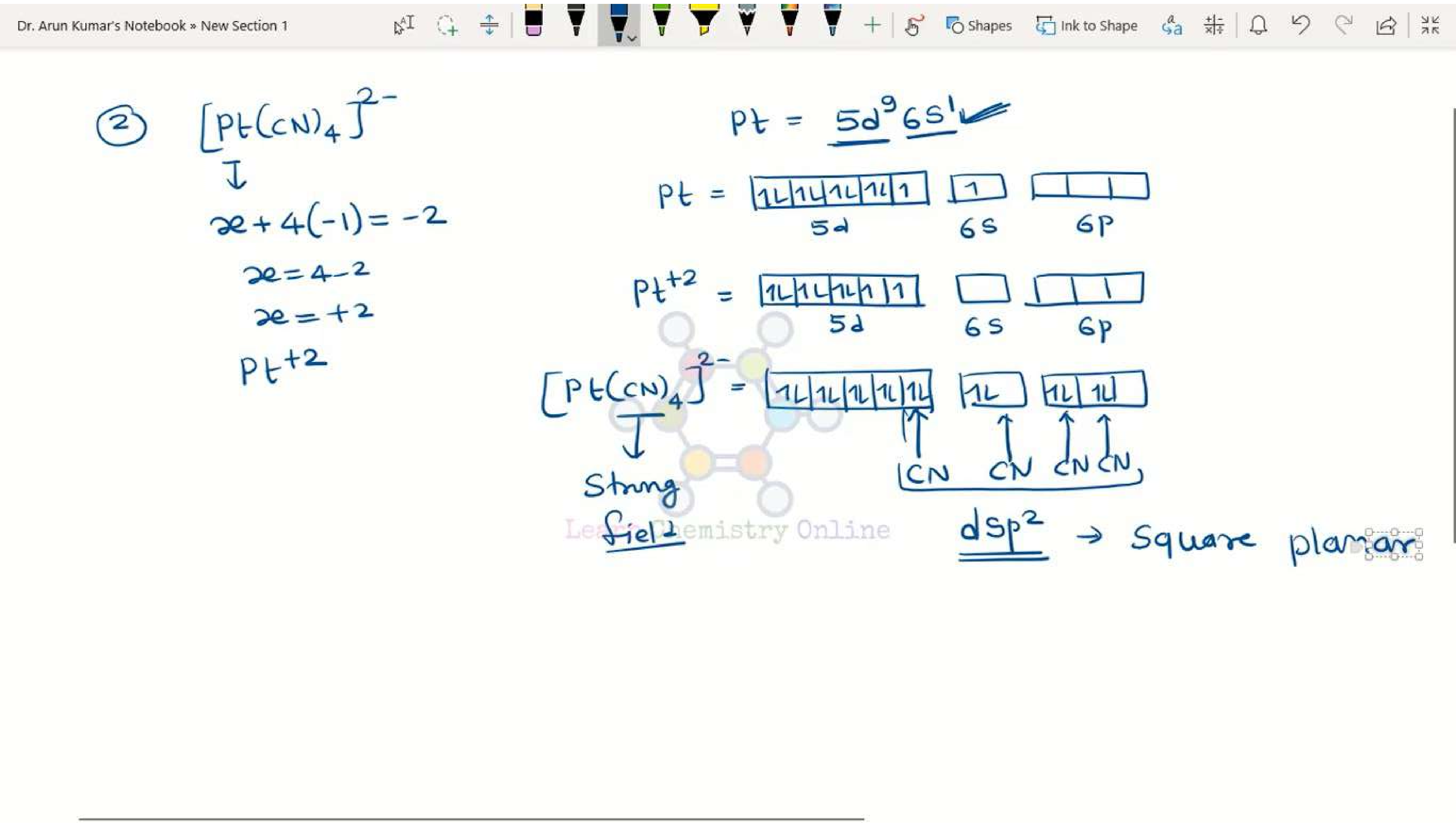
$x = +2$

Ni^{+2}

$Ni = 3d^8 4s^2$



dsp^2 - square planar



② $[Pt(CN)_4]^{2-}$

↓

$x + 4(-1) = -2$

$x = 4-2$

$x = +2$

Pt^{+2}

$Pt = \underline{5d^9}\,\underline{6s^1}$ ✓

$Pt = \underset{5d}{\boxed{\uparrow\downarrow|\uparrow\downarrow|\uparrow\downarrow|\uparrow\downarrow|\uparrow}}\ \underset{6s}{\boxed{\uparrow}}\ \underset{6p}{\boxed{\ \ |\ \ |\ \ }}$

$Pt^{+2} = \underset{5d}{\boxed{\uparrow\downarrow|\uparrow\downarrow|\uparrow\downarrow|\uparrow|\uparrow}}\ \underset{6s}{\boxed{\ \ }}\ \underset{6p}{\boxed{\ \ |\ \ |\ \ }}$

$[Pt(CN)_4]^{2-} = \boxed{\uparrow\downarrow|\uparrow\downarrow|\uparrow\downarrow|\uparrow\downarrow|\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow|\uparrow\downarrow|\ \ }$

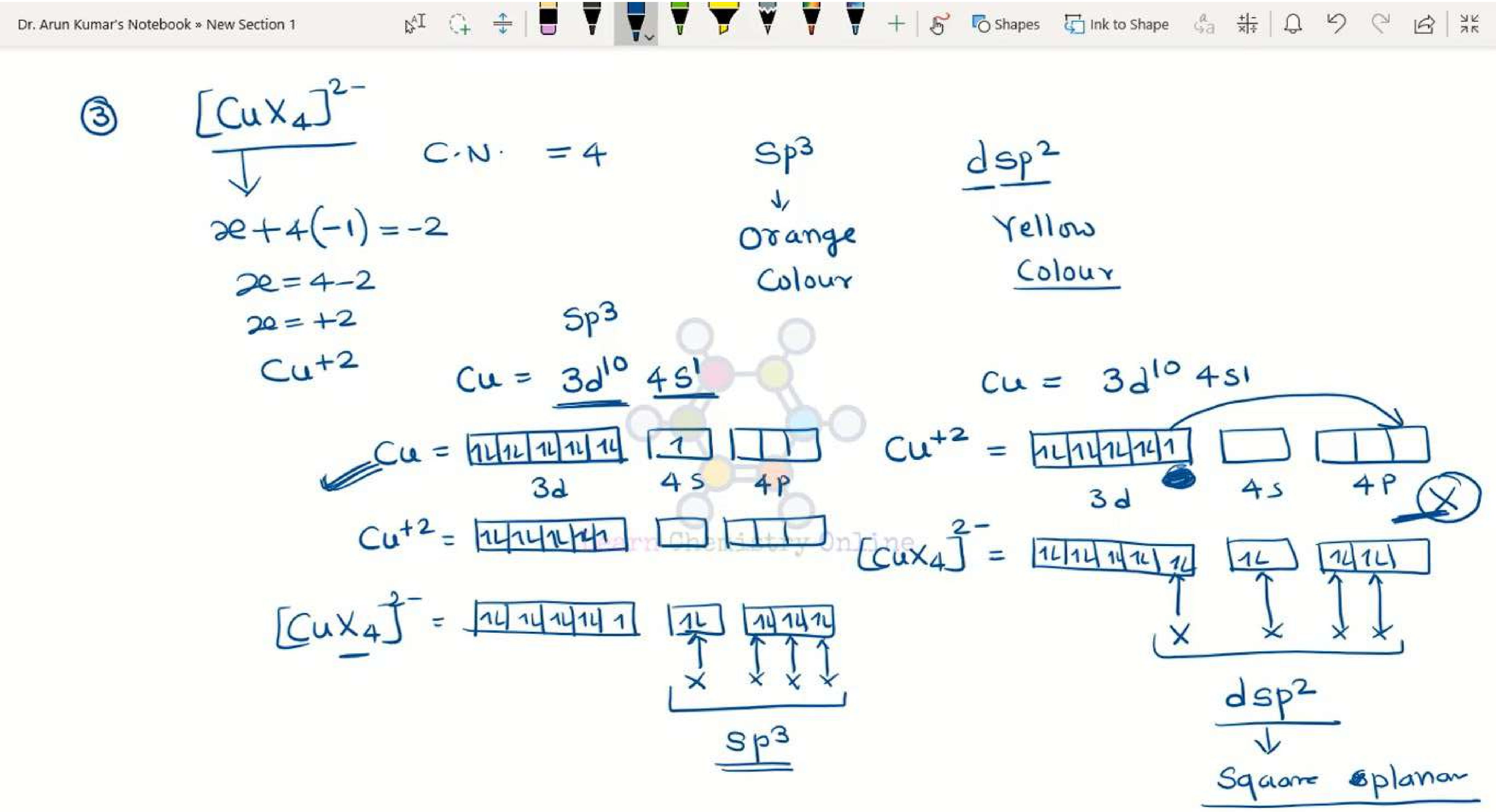
$\underbrace{CN\quad CN\quad CN\quad CN}$

↓

Strong

field

$\underline{\underline{dsp^2}}$ → Square planar



③ $[CuX_4]^{2-}$ C.N. = 4

$\downarrow$

$x + 4(-1) = -2$

$x = 4 - 2$

$x = +2$

Cu^{+2}

Sp³ ↓ Orange Colour

dsp² Yellow Colour

Sp³

Cu = $3d^{10}\ 4s^{1}$

Cu = [↑↓|↑↓|↑↓|↑↓|↑↓] [↑] [| |]
3d 4s 4p

Cu^{+2} = [↑↓|↑↓|↑↓|↑↓|↑] [ ] [| |]

$[CuX_4]^{2-}$ = [↑↓|↑↓|↑↓|↑↓|↑] [↑↓] [↑↓|↑↓|↑↓]
X X X X

Sp³

Cu = $3d^{10}\ 4s1$

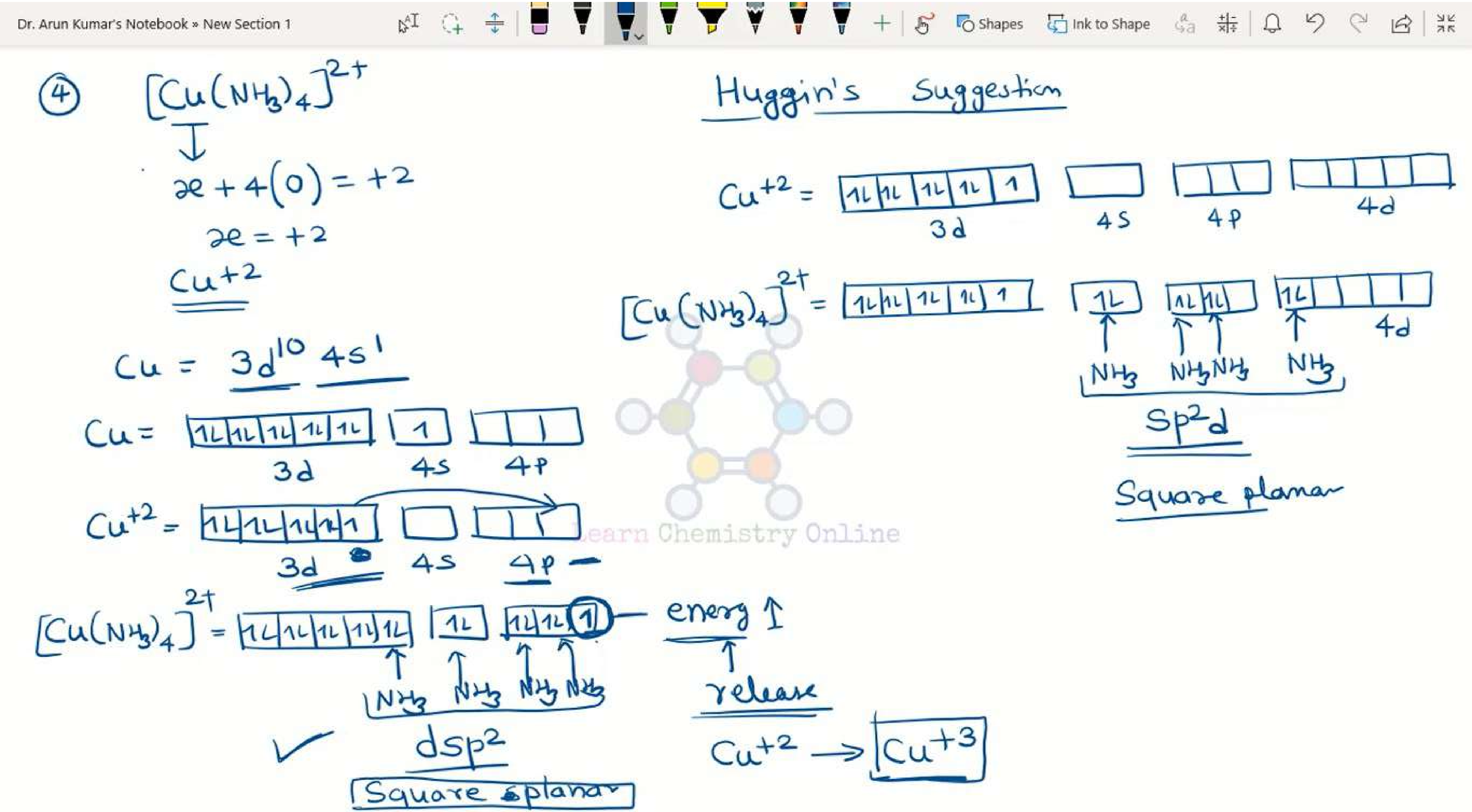
Cu^{+2} = [↑↓|↑↓|↑↓|↑↓|↑] [ ] [| |]
3d 4s 4P

$[CuX_4]^{2-}$ = [↑↓|↑↓|↑↓|↑↓|↑↓] [↑↓] [↑↓|↑↓|]
X X X X

dsp²

$\downarrow$

Square planar



④ $[Cu(NH_3)_4]^{2+}$

$x + 4(0) = +2$

$x = +2$

Cu^{+2}

$Cu = 3d^{10}\ 4s^1$

dsp^2

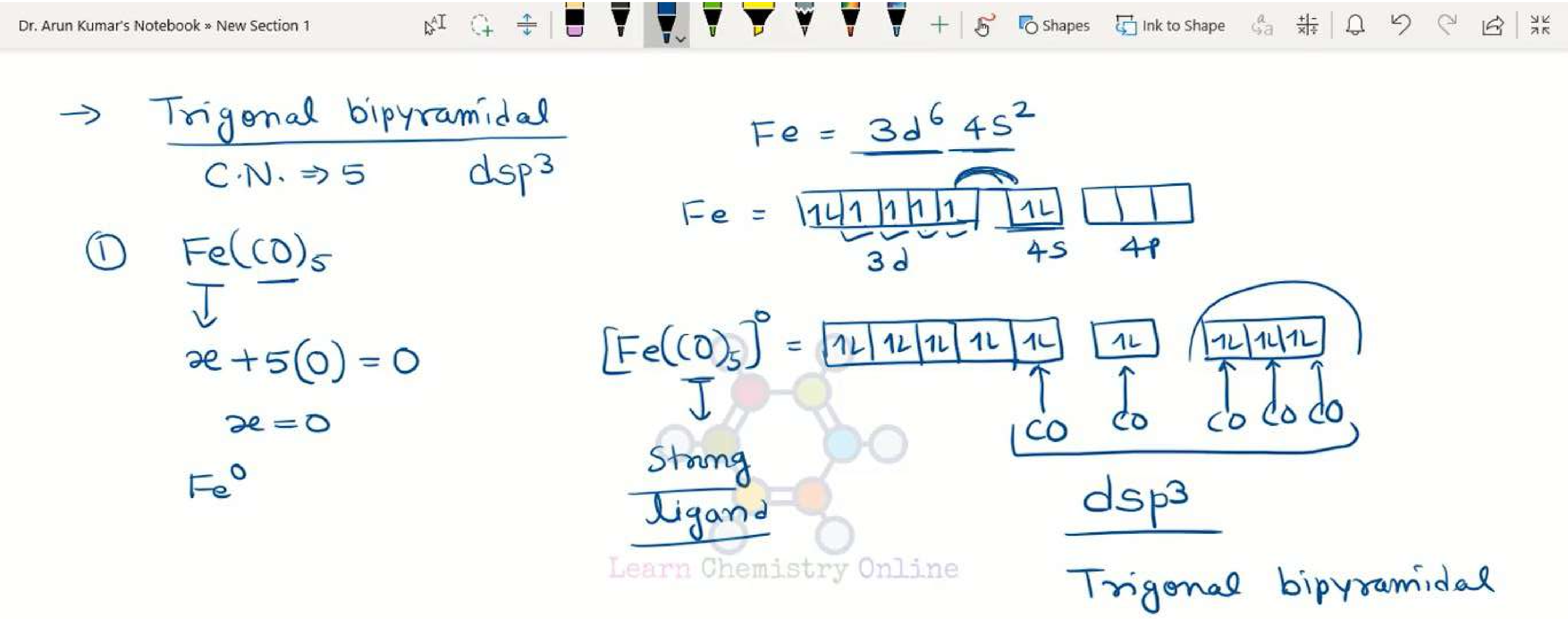
Square planar

$Cu^{+2} \rightarrow \boxed{Cu^{+3}}$

Huggin's Suggestion

sp^2d

Square planar



→ **Trigonal bipyramidal**

C.N. ⇒ 5 dsp^3

① $Fe(CO)_5$

↓

$x + 5(0) = 0$

$x = 0$

Fe^0

$Fe = \underline{3d^6}\ \underline{4s^2}$

$Fe = \underbrace{\uparrow\downarrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow}_{3d}\ \ \underbrace{\uparrow\downarrow}_{4s}\ \ \underbrace{\ \ \ \ \ \ }_{4p}$

$[Fe(CO)_5]^0 = \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \ \uparrow\downarrow\ \ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow$

↓   CO CO CO CO CO

Strong ligand

$\underline{dsp^3}$

Trigonal bipyramidal

→ **Application of VBT**

① To find out no. of unpaired e^- in given complex

n =

$\boxed{d^2sp^3}$ ↓ Strong ligand ↓ less no. of unpaired

$\boxed{sp^3d^2}$ ↓ weak ligand ↓ more no. of unpaired e^-

② To predict the type of hybridisation in Octahedral Complex

Octahedral

n = low ↓ d^2sp^3

n = high ↓ sp^3d^2

③ Geometry of complex

→ limitations of VBT

① does not explain relative Stability of complex

② Rate of reaction of metal complex

③ does not explain about inner & outer orbital complexes

④ fails to explain finer details of mag. properties

⑤ Cannot explain colour (spectra) of complex

⑥ does not explain formation of LS and HS complexes

⑦ does not explain about excitation of e− from 3d to 4p

———x———x———x———