SHODH JUNE 2024

Inorganic Chemistry

Bioinorganic Chemistry

Lecture No.- 05

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RECAP *of previous lecture*

1) Metalloenzymes

TOPICS *to be covered*

1) Electron Transfer System

The CORRECT combination for metalloenzymes given in Column I with their catalytic reactions in Column II is

Column I	Column II
(i) Cytochrome P-450	(K) $2H_2O_2 \rightarrow 2H_2O+O_2$
(ii) Catalase	(L) $R\text{-}CH_2OH+O_2 \rightarrow R\text{-}CHO+H_2O_2$ (R=alkyl or aryl)
(iii) Galactose oxidase	(M) $O_2+4H^++4e^- \rightarrow 2H_2O$
(iv) Cytochrome c oxidase	(N) $R\text{-}H+O_2+2e^-+2H^+ \rightarrow R\text{-}OH+H_2O$ (R=alkyl or aryl)

(a) (i)–(M); (ii)–(N); (iii)–(K); (iv)–(L)
(b) (i)–(N); (ii)–(L); (iii)–(K); (iv)–(M)
(c) (i)–(N); (ii)–(K); (iii)–(L); (iv)–(M)
(d) (i)–(M); (ii)–(K); (iii)–(L); (iv)–(N)

#Q The correct option for the metal ion present in the active site of myoglobin, hemocyanin and vitamin B_{12}, respectively, is

(a) iron, iron and zinc

(b) molybdenum, iron and copper

(c) iron, copper and cobalt

(d) molybdenum, copper and cobalt

#Q Match the iron and copper proteins with biological function in the table below: [CSIR NET FEB 2022] → 12 marks

Iron protein		Copper protein		Biological function	
A	Hemerythrin → O_2 transfer	i	Azurin	X	Oxygenase
B	Cytochrome P450	ii	Hemocyanin	Y	Electron transfer
C	Rieske protein	iii	Tyrosinase	Z	O_2 transport

4 marks

1. A-ii-Z, B-iii-X,C-i-Y
2. A-ii-Z, B-i-X, C-iii-Y
3. A-iii-Y, B-i-Z,C-ii-X
4. A-i-Y, B-iii-Z, C-ii-X

A - ii - Z

B - iii → X

C → i Y

Topic: Electron Transfer System

- Fe-S system

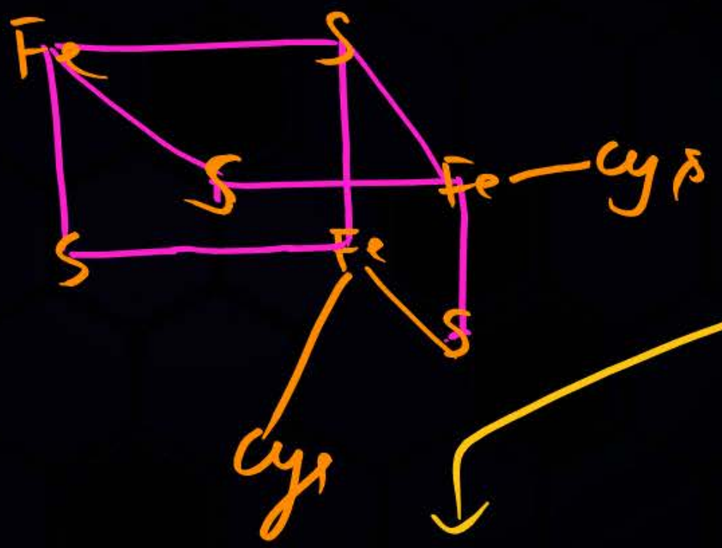
- Ruberdoxin
- Ferridoxin
  - Fe_2S_2
  - Fe_3S_4
  - Fe_4S_4

3 Fe Ferridoxin :

No of labile S = 4

4 marks
No of labile S & cysteine ligand ?

(a) 3, 3
(b) 3, 4
(c) 4, 3 ✓
(d) 4, 4



Redox Form

O.F

$Fe(III)\ Fe(III)\ Fe(II)$

Para

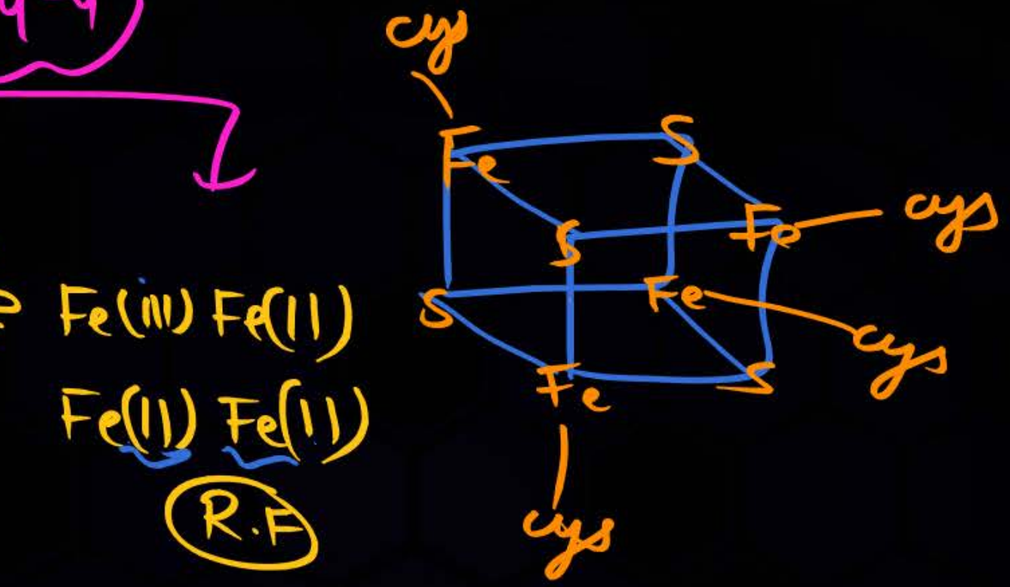
$\rightleftharpoons$

R.F

$Fe(III)\ Fe(II)\ Fe(II)$

Para

4 Fe Ferredoxin: Fe_4S_4



$Fe^{(III)}$ $Fe^{(III)}$ $Fe^{(II)}$ $Fe^{(II)}$ ⇌ $Fe^{(III)}$ $Fe^{(II)}$ $Fe^{(II)}$ $Fe^{(II)}$

O.F

R.F

Dia

Para

Labile S can be identified by treating with acid

→ $H_2S\uparrow$

[CSIR NET DEC-2015]

#Q The biological functions of cytochrome P_{450} and myoglobin are, respectively:

1. Oxidation of alkene and O_2 storage
2. O_2 transport and O_2 storage
3. O_2 storage and electron carrier
4. Electron carrier and O_2 transport

#Q Which of the following statements for rubredoxin [CSIR NET FEB 2022]

A. Fe^{2+} center has a tetrahedral geometry.

B. Reduced form of iron is diamagnetic.

C. Fe^{2+} center undergoes Jahn-Teller distortion.

D. It is a [2Fe–2S] cluster.

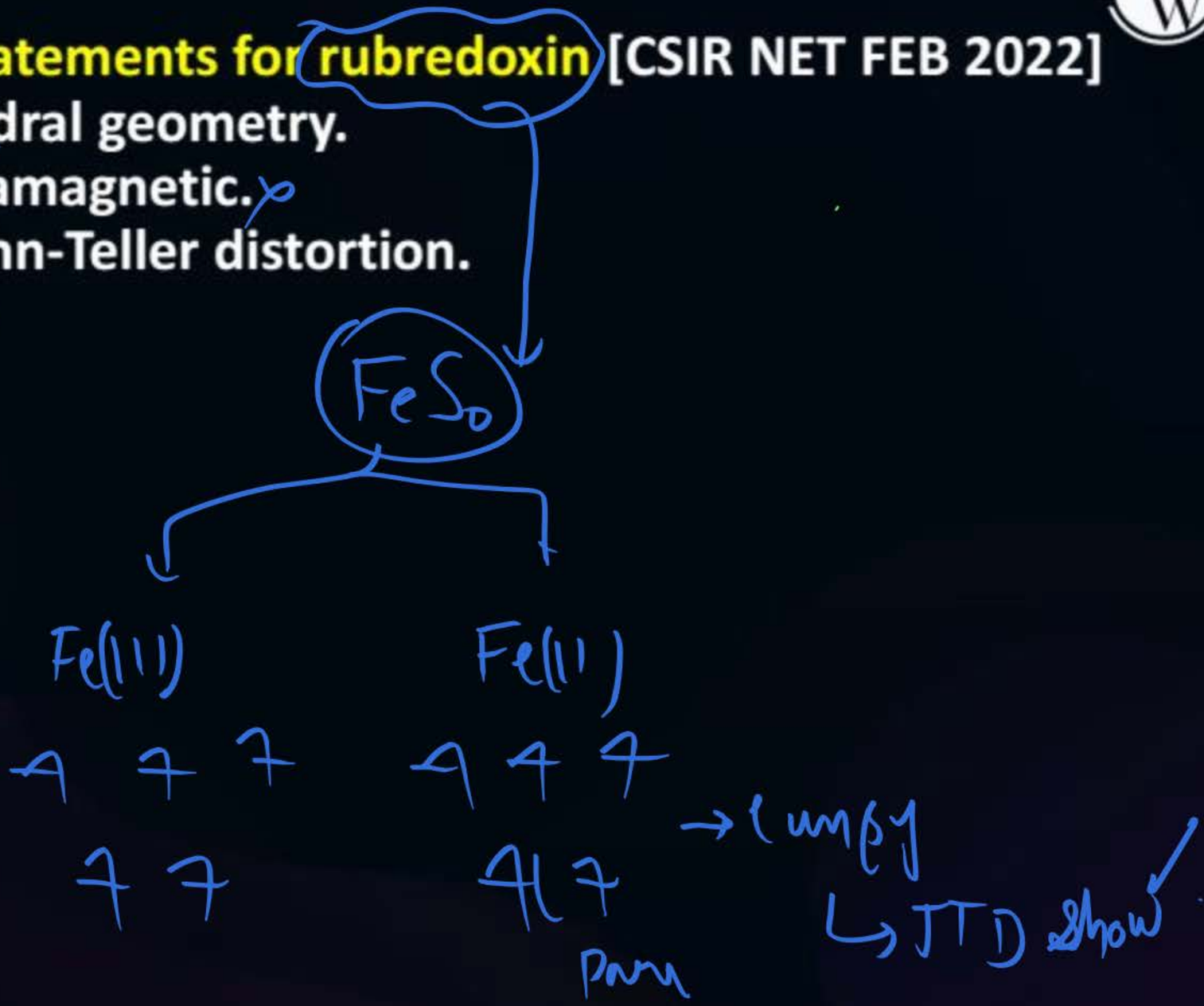
are correct?

(1) A, B and C

(2) A, C and D

(3) C and D only

(4) A and C only



#Q The number of inorganic sulfides in cubane like ferredoxin and their removal method, respectively, are: **[CSIR NET JUNE-2017]**

(1) eight and washing with an acid

(2) four and washing with a base

(3) eight and washing with a base

(4) four and washing with an acid

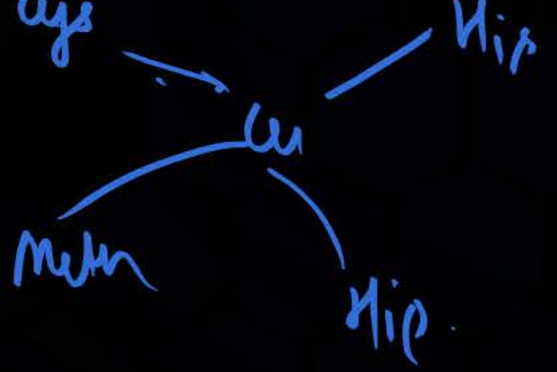
Blue copper protein

Plastocyanin

↓

$e^{\ominus}$ transfer in plants.

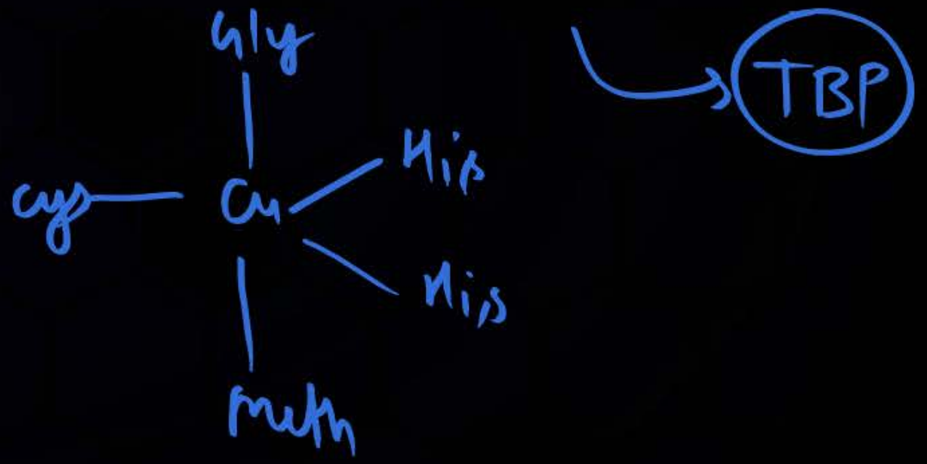
- Flattened td / Distorted td
- C_{3v}
- Geo in between td & square planar.



Azurin

↓

$e^{\ominus}$ transfer in bacteria.



Cytochromes

- involve in $e^{\ominus}$ transfer
- Heme unit.
- $Fe(III) \rightleftharpoons Fe(II)$
- oh enviro, L.S

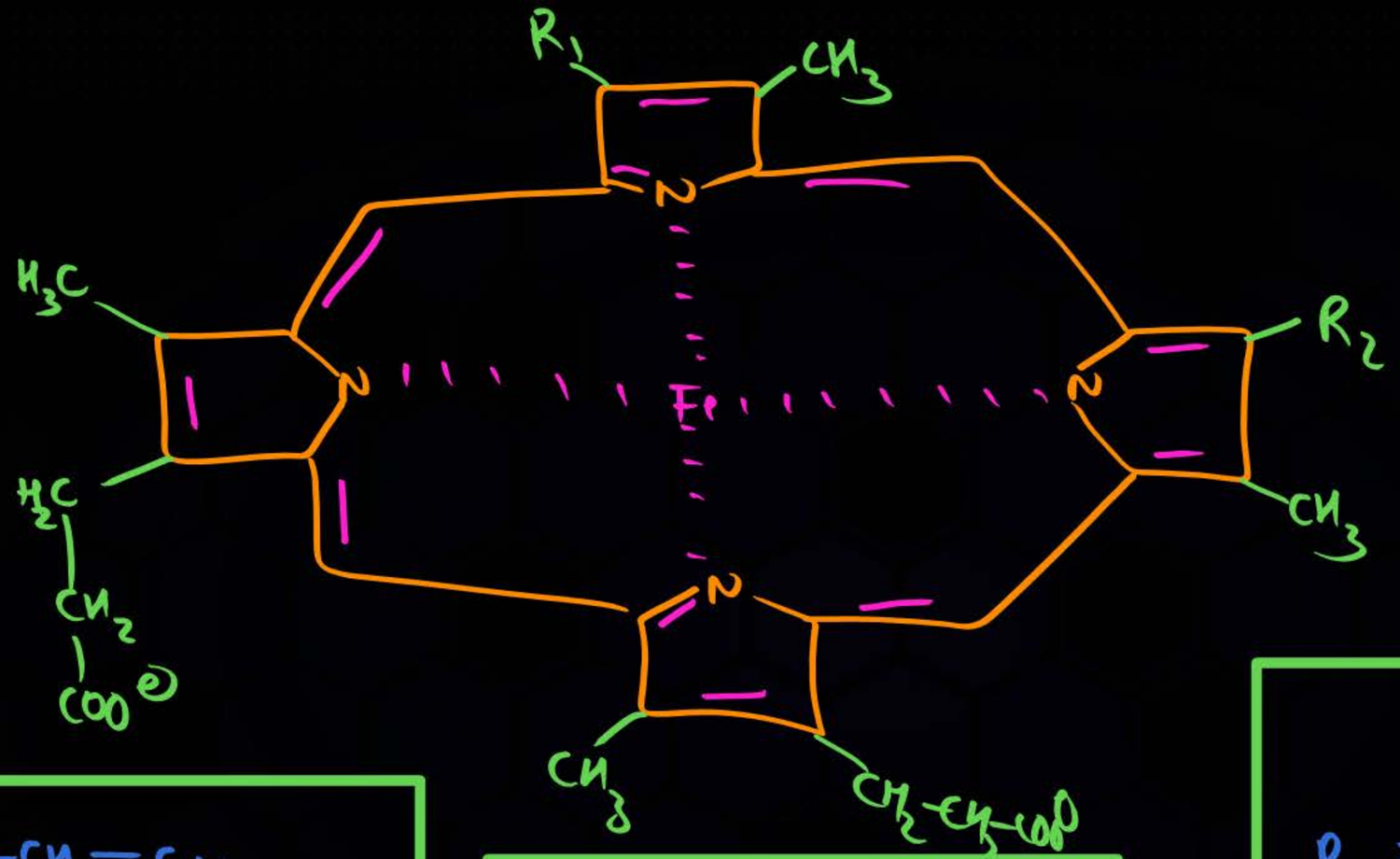
O.F	R.F
$Fe(III) \rightleftharpoons$	$Fe(II)$
- -	- -
π π π	π π π π
Para	Dia

There are different cytochrom. like cyt(a), cyt(b) & cyt(c) which are differentiate on the basis of ligand attached to their Heme group.

cyt(a) ↓ Heme(a)

cyt(b) ↓ Heme(b)

cyt(c) ↓ Heme(c)



$R_1 = -CH=O$

$R_2 = -CH=CH_2$

→ Chlorohemes

$R_1 = -CH=CH_2$

$R_2 = C_{18}H_{30}OH$

↓

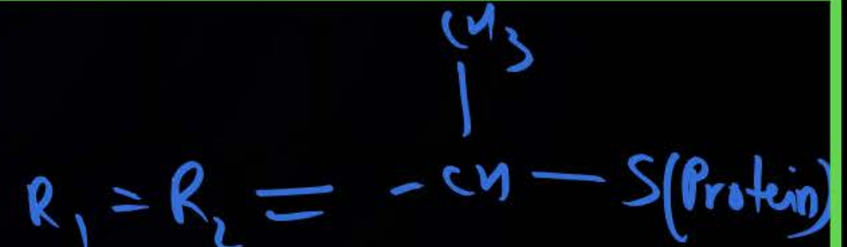
Heme(a) → cyt(a)

$R_1 = R_2 = -CH=CH_2$

↓

Heme(b) → cyt(b)

(Protoporphyrin(IX))

$R_1 = R_2 =$ 

↓

Heme(c) → cyt(c)

Acc different groups attached to the Heme group of cytchromes. So these cyt have diff Oxidation potential.

O.P → cyt(b) > cyt(c) > cyt(a)

Flow of $e^{\ominus}$ transfer → cyt(b) → cyt(c) → cyt(a)

- Porphyrin
- Metalloporphyrin
- Myoglobin
- Hemoglobin
- Cooperative effect.
- Bohr effect.
- curve
- Keratin
- met-Hem

- Hemerythrin.
- Hemocyanin
- Metalloen

- Metal Storage / Metal
- Nitrogen Fixation
- Photosynth

Intensity order:

- $[NiCl_4]^{2\ominus}$ $[Ti(H_2O)_6]^{3+}$ $[CrO_4]^{2\ominus}$ $[Mn(H_2O)_6]^{2+}$

  CrO_4 ↓ LMCT

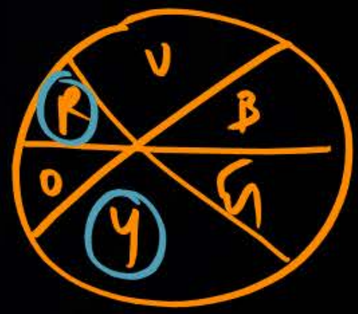
  $Mn(H_2O)_6$ ↓ d^5 (HS) → S.F, L.F

$$[CrO_4]^{2\ominus} > [NiCl_4]^{2\ominus} > [Ti(H_2O)_6]^{3+} > [Mn(H_2O)_6]^{2+}$$

- Complex A is yellow and complex B is red
  - A: yellow ↓ violet
  - B: red ↓ green

Δ_o ?

$\Delta_o \rightarrow A > B$



V B G Y O R

$\uparrow E$ $\downarrow \nu$

$\uparrow \Delta_o$ $\downarrow \nu$

○ Which of the following will not exhibit optical isomerism?

(a) $[Co(en)_3]^{3+}$ → Act

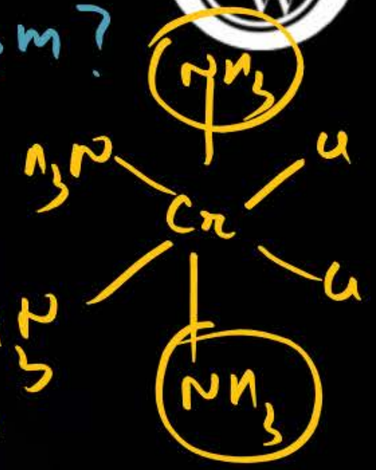
(b) $[Cr(ox)_3]^{3+}$ → Act

(c) cis-$[Co(en)_2Cl_2]$ → Act

(d) $[Co(NH_3)_3Cl_3]$ → OIn

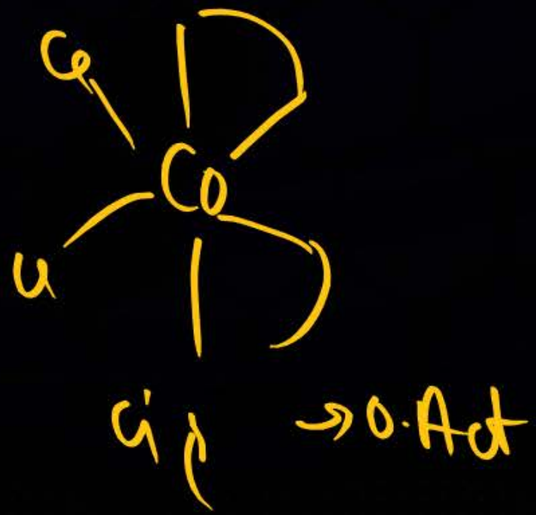
(e) $[PtCl_2(NH_3)_2]$ ← S.Plan ← OIn

(f) cis-$[Cr(NH_3)_4Cl_2]$ → OIn



(g) trans-$[Cr(NH_3)_4Cl_2]$ → OIn

(h) trans-$[Co(en)_2Cl_2]$ → OIn.



Cis → Act

Cl → OInAct

d, e, f, g, h

2 mins Summary

1) Electron Transfer System

2 mins Summary

Topic Metalloenzymes

Topic Electron Transfer System


Thank
you