Nomenclature of Complexes –

Two things to remember –

1. Name of cation and then anion. (irrespective of complex formation).
2. Naming of the complex position.
   - (a) No. of ligands (di, tri, tetra, or necessary bis, tris, tetrakis etc.)
   - (b) Naming of ligands in alphabetical order. (anionic ligands will end with the letter 'O'. Other ligands will be named as such except ammonia – ammine, water → aquo. (aqua), CO – carbonyl, NO – Nitrosyl
   - (c) If the complex is anionic, the metal will end with letter 'ate' Otherwise the metal will be named as such.
   - (d) The oxidation state of metal will be written in Roman letter in parentheses.

$[Pt(C_5H_5N)(NO_2)Cl(NH_3)]$ – Amminechloronitro pyridine platinum (II)

$K_2[Pt(C_2H_4)Cl_3]$ → Potassium trichloroethylene platinate (II).
Zeise's salt.

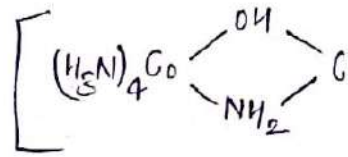
$[Pt(NH_3)_4][PtCl_4]$ → Tetraammineplatinum (II) tetrachloroplatinate (II).

$[Pt(NH_3)_4Cl_2][PtCl_4]$ → Tetraamminedichloroplatinum (IV) tetrachloro platinate (II).

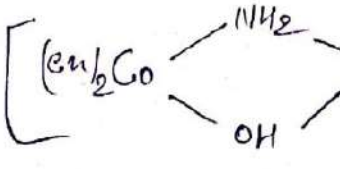
$[Co(NH_3)_6][Cr(SCN)_6]$ → Suppose that No. of Co & Cr oxidation state same. +3.
Hexaammine cobalt (III) hexathiocyanatochromiate (III).

$[Co(NH_3)_6][Cr(SCN)_6]$ → Suppose Co is in +2 and Cr is in +4 state.
Hexaammine cobalt (II) hexacyanochromate (IV).

$[Co(NH_3)_3Cl_3]$ → Triammine trichloro cobalt (III).



Bis tetraammine – μ – amido – μ – hydroxo dicobalt (III) chloride.
OR.
Octaammine – μ – amido – μ – hydroxo dicobalt (III) chloride.



Tetakis (ethylenediamine) – μ – amido – μ – hydroxo dicobalt (III) sulphate.
OR.
Bis (ethylenediammine) – μ – amido – μ – hydroxo – di cobalt (III) sulphate.

$[(H_3N)_5Co-O_2^{2-}-Co(NH_3)_5](NO_3)_4$.

bis[(pentaammine)cobalt(III)] - μ-peroxo-nitrate.

OR.

bis(pentaammine)-μ-peroxodicobalt(II) nitrate.

Bis(ethylenediammine)cobalt(III)-μ-amido-μ-peroxo-bis(ethylenediammine) cobalt(III) nitrate.

$[(H_3N)_5Co-O_2^{-1}-Co(NH_3)_5](NO_3)_5$.

bis(pentammine)-μ-superoxo-dicobalt(III) nitrate.

$[Cl(NH_3)_4-Co-O_2-Co(NH_3)_5](NO_3)_4$.

Tetraammine chloro cobalt(III)-μ-superoxo-pentaammine cobalt(III) nitrate.

$[(H_3N)_5Co(NH_2)Co(NH_3)_5](NO_3)_5$

bis(pentaammine)-μ-amido dicobalt(III) nitrate.

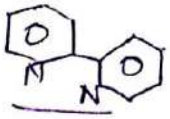
- $K_4[Fe(CN)_6]$ - Potassium hexacyano ferrate(II)

  $K_3[Fe(CN)_6]$ - Potassium hexacyano ferrate(III).

$[Co(C_5H_5N)_2(NH_3)_4](NO_3)_3$ - tetraammine bis(pyridine) cobalt(III) nitrate.

$[Co(C_{10}H_8N_2)(NH_3)_4](NO_3)_3$ - tetraammine bipyridine cobalt(III).

Pyridine



bipyridine.

Isomerism In Coordination Compounds –

"Substances having same chemical formulae but different structural arrangements, are called isomers and the phenomenon is known as isomerism." (Structural & Stereoisomerism)

Because of the complicated formula of many coordination compounds and a variety of bond types, and no. of shapes possible, many different types of isomerisms occur Werners classification - Polymerization, Ionization, Hydrate, Linkage, Coordination, Coordination position, Geometrical and Optical isomerism.

This is the general classification accepted.

(1) Polymerization Isomerization - It occurs between compounds having same empirical formula but different molecular weights. For eg.

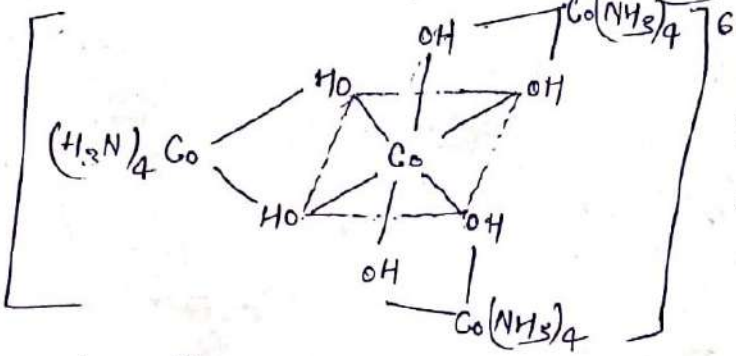
① $[Pt(NH_3)_2Cl_2]$ ⇒ empirical formula.

$[Pt(NH_3)_4][PtCl_4] \Rightarrow Pt_2(NH_3)_4Cl_4$

$[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2 \Rightarrow Pt_3(NH_3)_6Cl_6$

$[Pt(NH_3)_3Cl]_2[PtCl_4] \Rightarrow Pt_3(NH_3)_6Cl_6$

② $\left[(NH_3)_3Co\begin{matrix}OH\\OH\\OH\end{matrix}Co(NH_3)_3\right]^{3+}$ and $\left[Co\left\{\begin{matrix}OH\\OH\end{matrix}\right\}Co(NH_3)_4\right]_3^{6+}$



It is due to different nuclei in the compounds.

(2) Ionization Isomerism ⇒ It is due to the exchange of groups between the complex ion and the ions outside it eg.

① $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$.
(Red violet) (Red.)

② $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

③ $[Co(en)_2(NO_2)Cl]SCN$, $[Co(en)_2(NO_2)(SCN)]Cl$ & $[Co(en)_2Cl(SCN)]NO_2$.

(3) Hydrate Isomerism – It is due to replacement of anionic ligands by water molecule of ionisation isomers. It is a special kind of ionisation isomerism.

eg. Three isomers of $CrCl_3 \cdot 6H_2O$ are known. From conductivity measurements and quantitative precipitation of chloride ions, they have the following formula –

$[Cr(H_2O)_6]^{3+} Cl_3$ (violet) 3 ionic Cl^-

$[Cr(H_2O)_5Cl] Cl_2 \cdot H_2O$ (green) 2 ionic Cl^-

$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (green) 1 ionic Cl^-

(4) Linkage Isomerism → Also called structure isomerism.

Certain ligands contain more than one atom. which can donate electron pair to central atom Such ligands are called ambidentate ligands. In NO_2^- ion either N or O atom could act as the electron pair donor (I) Two different complexes of $[Co(NH_3)_5NO_2]Cl_2$ have been prepared. These are –

To (i) $[Co(NH_3)_5ONO]Cl_2$ (red)

O bonded nitrito compound.

It is easily decomposed by acid to give HNO_2.

(ii) $[Co(NH_3)_5NO_2]Cl_2$ (Yellow).

N- bonded nitro compound

It is not decomposed by acid.

(II) In SCN^- ion either S and N could act as electron pair donor –

$[Zn(SCN)_4]^{2-}$ and $[Zn(NCS)_4]^{2-}$

(5) Coordination Isomerism – It is extreme case of ionization isomerism. when both the positive and negative ions are complexed This isomerism may be caused by the interchange of ligands between the anion and cation complexes. For eg –

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

I II

In complex I NH_3 is coordinating through Co and CN^- ion through Cr but in compound II, this is vice-versa.

② $[Cu^{II}(NH_3)_4][Pt^{II}Cl_4]$ and. $[Cu^{II}Cl_4][Pt^{II}(NH_3)_4]$

③ $[Pt(NH_3)_4Cl_2]PtCl_4$. and. $[Pt(NH_3)_4Cl_2][PtCl_4]$

⑥ Coordination Position – In polynuclear complexes as inter-change of ligands between the different metal nuclei, to give rise to coordination positional isomerism.. For eg. Bridging OH – may be

$[(H_3N)_4Co(NH_2,O_2)Co(NH_3)_4Cl_2]Cl_2$ & $[Cl(NH_3)_3Co(NH_2,O_2)Co(NH_3)_3Cl]Cl_2$.

⑦ Stereo isomerism –

Coordination No. 4 :- There are two principle geometry:

① Tetrahedral. ② Square Planar. (Tetragonal).

⇒ Stereochemistry among tetrahedral complexes –

Geometrical isomerism ⇒ Not possible in tetrahedral complexes.

Optical isomerism –

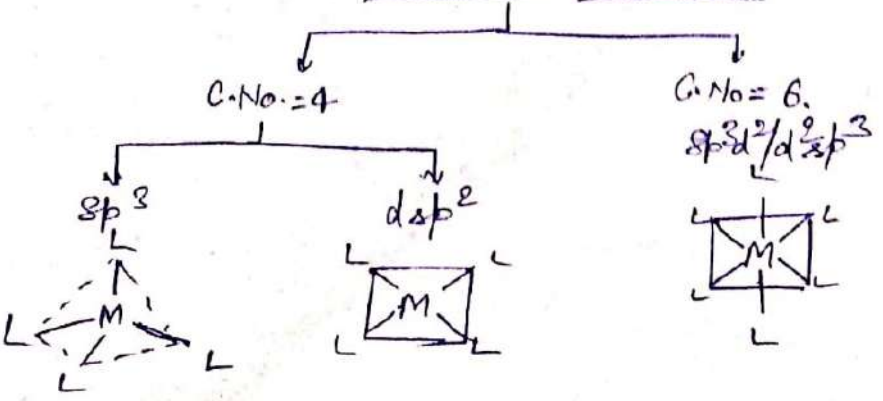
(i) If compound contains centre of inversion, the compound will be optically inactive.

(ii) If symmetry of plane is present, the compound will also be optically inactive.

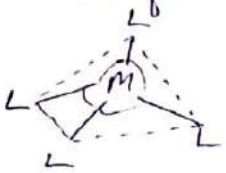
(iii) If both (plane of symmetry and centre of inversion) are absent then compound may be optically active.

Optical isomerism is possible only in those tetrahedral complexes in which central atom is bounded with four different groups and complexes are called asymmetric.

Geometrical Isomerism

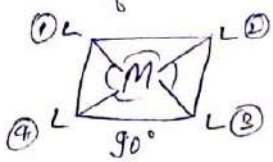


(i) In case of C.No. = 4. Tetrahedral complex.



due to symmetrical distribution of ligands around central atom. } They will not show G.I.

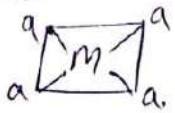
(ii) In case of C.No. = 4. Square planar complex.



cis-position (90°) [(1,2) (2,3) (3,4) (4,1)] ⇒ 4

trans-position (180°) [(1,3), (2,4)] ⇒ 2
(opposite)

(1) $[Ma_4]^{n\pm}$ → Monodentate ligand.



G.I. ✗

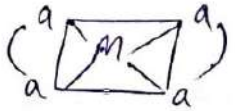
(2) $[Ma_3b]^{n\pm}$ or $[Mab_3]^{n\pm}$

G.I. ✗ a-b = 180°, a-a = 180°

Any arrangement give same structure.

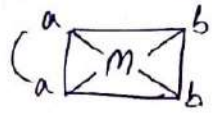
(3) $[M(aa)_2]^{n\pm}$ Symmetrical bidentate ligand.

Bidentate ligands atoms bind at cis-positions. not at trans.



G.I ✗

(4) $[M(aa)b_2]$ (Bi, Mono)



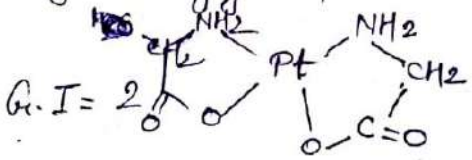
G.I. ✗

(5) $[M(aa)bc]$

G.I. ✗

$[M(ab)_2]$ = ab bidentate ligand.

eg. cis-diglycinatoplatinum(II)

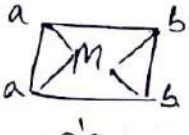


G.I = 2

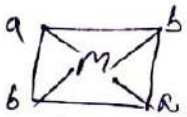
cis - trans

(6) $[Ma_2b_2]^{n\pm}$

eg. $[Pt(NH_3)_2Cl_2]$ cis- and trans-platin.

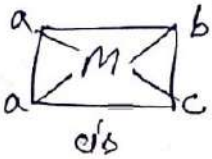


cis

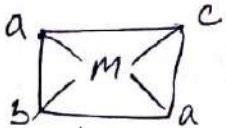


trans.

(7) $[Ma_2bc]^{n\pm}$



cis

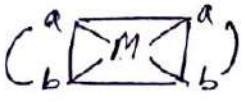


trans.

G.I. = 2

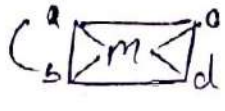
eg. $[Pt(Py)_2NH_3Cl]$

(8) $[M(ab)_2]^{n\pm}$ Unsymmetrical bidentate ligand.



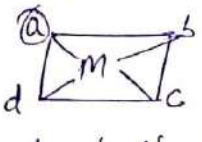
G.I. = 2

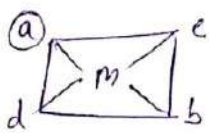
(9) [M(ab)cd]

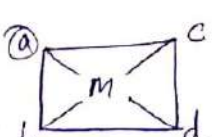


G.I = 2

(10) $[M(abcd)]^{n\pm}$ 3- isomers.





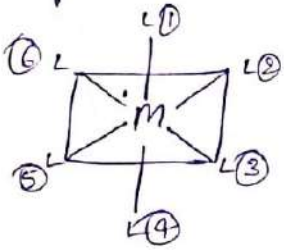


G.I. = 3

If d, e, or b is fixed, same structures will be repeated. only 3- isomers are possible

eg. $[Pt(NH_3)NO_2(Py)NH_2OH]$

(11) In case of C.No. 6, Octahedral Complexes.



Square bipyramidal. ① & ④ above and below the plane.

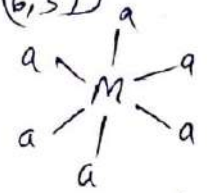
① with ② ③ ⑤ ⑥ – at 90°

④ with ⑤ ⑥ ② ③ – at 90°

cis- positions. (90°) - [(1,2)(1,3)(1,5)(1,6),(4,3)(4,5)(4,2) (4,6)(2,3)(3,5)(5,6)(6,2)] – 12 – G.I. position

trans- positions [(1,4)(2,5)(6,3)]

(i) $[Ma_6]^{n\pm}$ → Monodentate



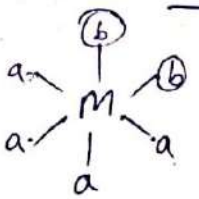
G.I = 0.

(ii) $[Ma_5b]^{n\pm}$ or $[Mab_5]^{n\pm}$

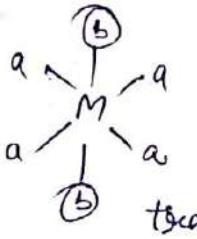
All six bonds identical.

G.I. = 0.

(iii) $[Ma_4b_2]^{n\pm}$ Ref.



cis-



trans.

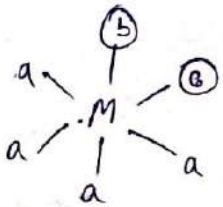
G.I = 0

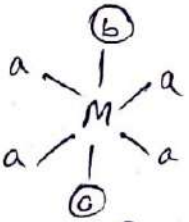
eg. $[CrCl_2(NH_3)_4]^+$

cis-violet

trans- green.

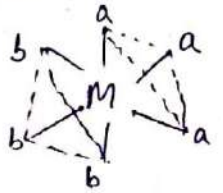
(iv) $[Ma_4bc]$ Ref.





G.I. = 2

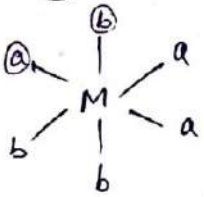
$[Ma_3b_3]^{n\pm}$



All a & b are in front of each other.

a-b
a-b
a-b

→ facial isomer 'Fac' isomer.



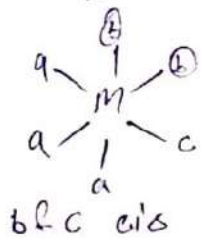
a-b
a-a
b-b

Meridional or 'Mer' isomer.

eg. $[Rh(Py)_3Cl_3]$ fac- mer isomer.

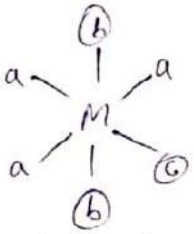
$[Ma_3b_2c]^{tn}$

G.I. = 3

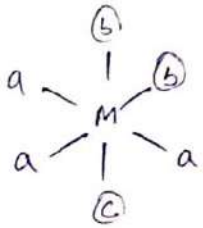


b & c cis

b & b cis.



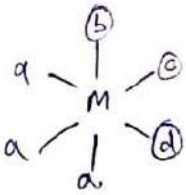
b & b trans.

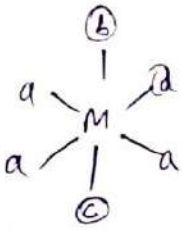


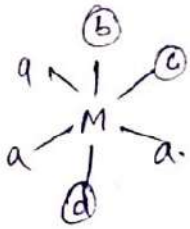
b & c trans.

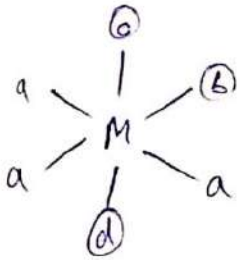
$[Ma_3bcd]^{nt}$

G.I = 4



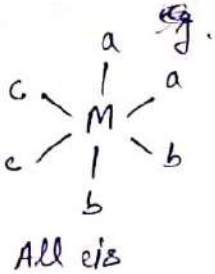




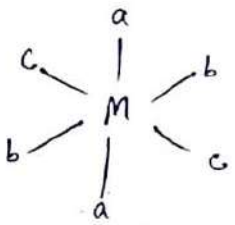


$[Ma_2b_2c_2]^{nt}$

eg.

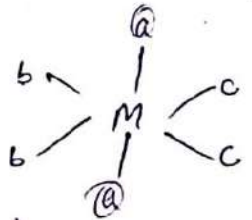


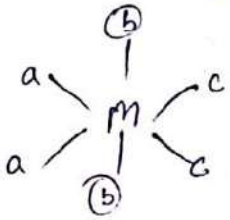
All cis

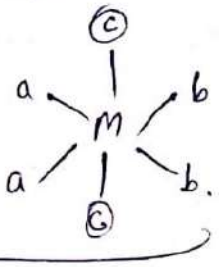


All - trans.

G.I = 5

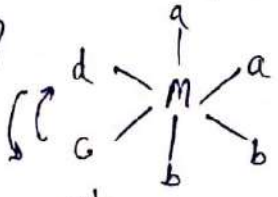




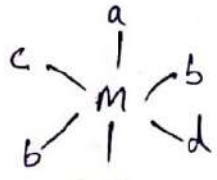


Trans.

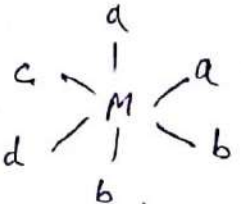
$[M(a_2b_2cd)]$



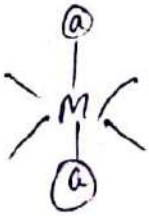
cis.

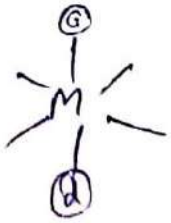


Trans.

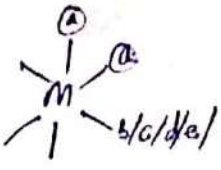


cis.





$[M(a_2bcde)]$

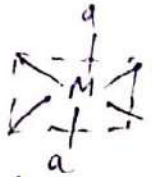


(b) → c,d,e → 3 arrange

(b,c) → d,e → 2

(b,c,d) → e → 1

cis (6)



trans - (3)

Total = G.I. = (9)

facial & meridional. - Meridional is ff mixed cis-trans isomerism.

If 3- ligand in one plane

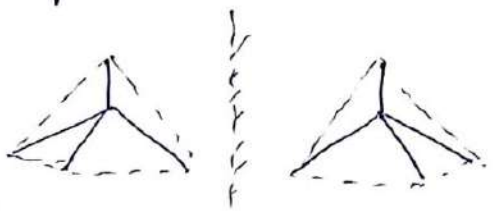
$[Co Cl_3(NH_3)_3]$ 3-NH_3 in one plane.

Optical Isomerism - Rotate the plane polarized light - optically active.

- Substances mirror image & should not superimpose.
- Plane of symmetry should not present.

C.No. 4.

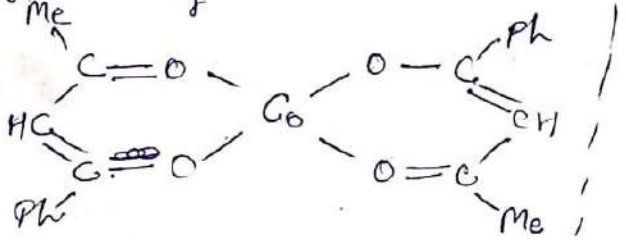
Tetrahedral -



Non-superimposible.

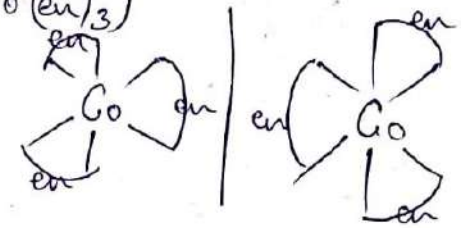
Sq. planar. ✗ due to plane of symmetry.

eg.



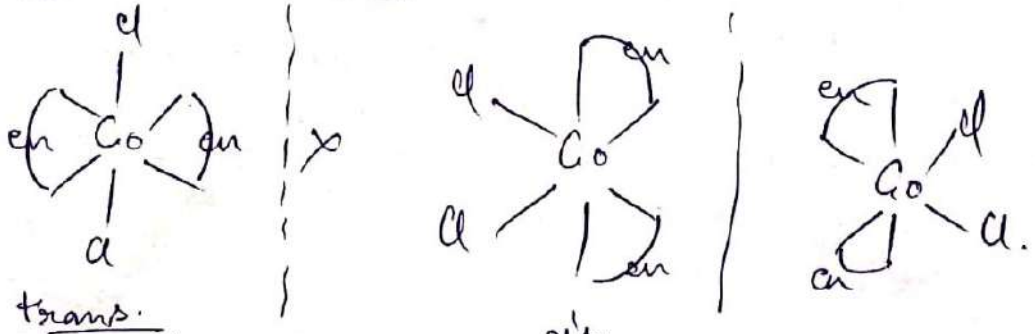
C.No. 6

(a) $[M(aa)_3]$ $[Co(en)_3]^{3+}$.



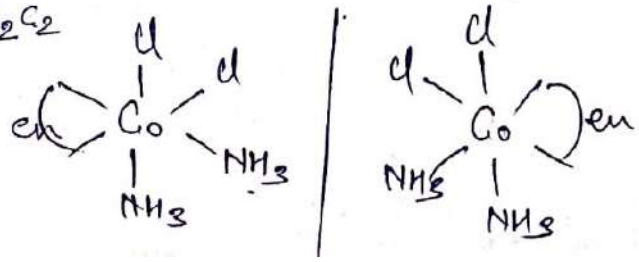
$[Cr(C_2O_4)_3]^{3-}$

(b) $[M(aa)_2b_2]$ or $[M(aa)_2bc]$

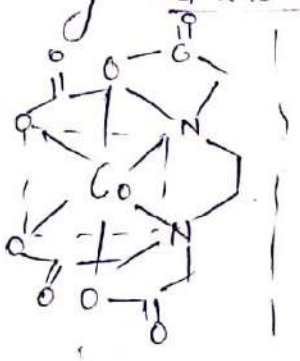


trans. cis

(c) $M(aa)b_2c_2$



(d) Complex containing hexadentate — $[Co(EDTA)]^-$ complex



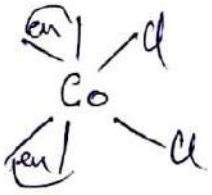
(e) Mabcdef → Geometrical = 15
All are optically active.

Mabcd - Tetrahedral.
Optically active. but not isolated due to labile nature of ligands.

Λ Lambda. Δ Delta.

Δ is used when two right hand propellar twist formed by bidentate ligand.

Λ is used when two left handed propellar twist present.



Λ - left handed propellar twist.

Δ right handed propellar twist