CHAPTER 2: METAL LIGAND BONDING IN TRANSITION METAL COMPLEXES

- Isomerism in Inorganic Complexes
- Geometrical
- Optical
- Structural
- Coordination position
- MOT
- MOT for Octahedral Complexes
- Merits & Demarits

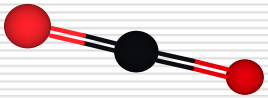
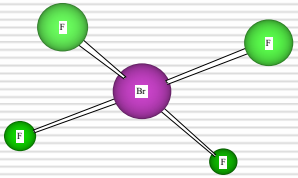
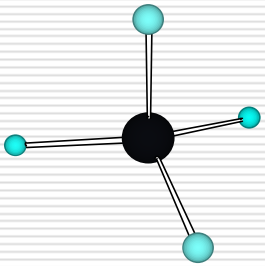
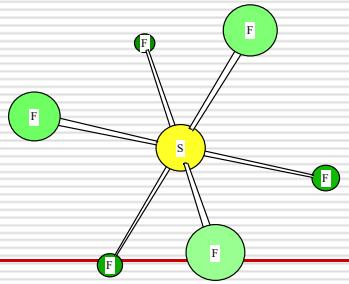
Chapter 2: Metal Ligand Bonding in Transition Metal Complexes

- Geometry?
- Coordination?
- Whether any linking between two?

Relation between CN Hybridization & Geometries

C N	Hybridization	Electron-group geometry	Examples
2	sp	Linear	$BeCl_2$
3	sp^2	Trigonal planar	BCl_3
4	sp^3	Tetrahedral	$SiCl_3$
5	dsp^2	Square planar	$CuCl_4$
6	dsp^3	Trigonal bipyramidal	PCl_5
7	d^2sp^3	Octahedral	$Ni(NH_3)_6$
8	d^3sp^3	Pentagonal bypyramidal	IF_7

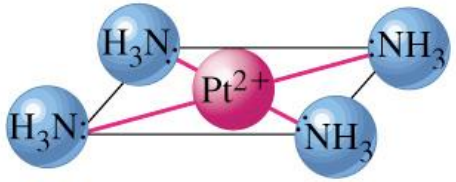
GEOMETRY & CN More examples

CN	Shape		Example
2	Linear		$[CuCl_2]^-$, $[Ag(NH_3)_2]^+$, $[AuCl_2]^-$
4	Square Planar		$[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$
			$[Pt(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$
4	Tetrahedral		$[Cu(CN)_4]^{3-}$, $[Zn(NH_3)_4]^{2+}$
			$[CdCl_4]^{2-}$, $[MnCl_4]^{2-}$
6	Octahedral		$[Cu(H_2O)_6]^{3+}$, $[V(CN)_6]^{4-}$,
			$[Cu(NH_3)_4Cl_2]^{+}$, $[Co(en)_3]^{3+}$

Geometry & C.N

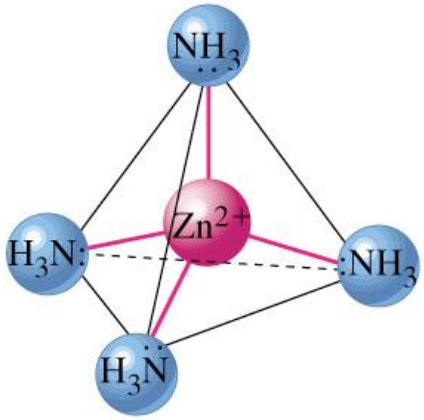
Linear

$Ag(NH_3)_2$



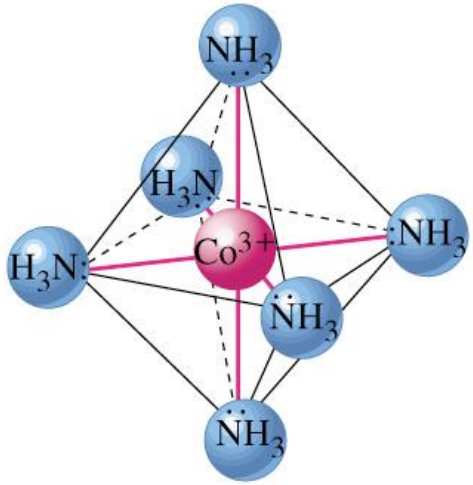
Square planar

$Pt(NH_3)_4$



Tetrahedral

$Zn(NH_3)_4$



Octahedral

$Co(NH_3)_6$

ISOMERISM

Isomers: Two compounds having same molecular formula but different arrangement of their atoms in space are called isomers of each other.(They may differ in properties & structures)

Isomerism: The phenomena is called Isomerism.

Examples: C_2H_6O compounds

There exist two compounds

CH_3CH_2OH and CH_3OCH_3

Ethyl Alcohol Acetone

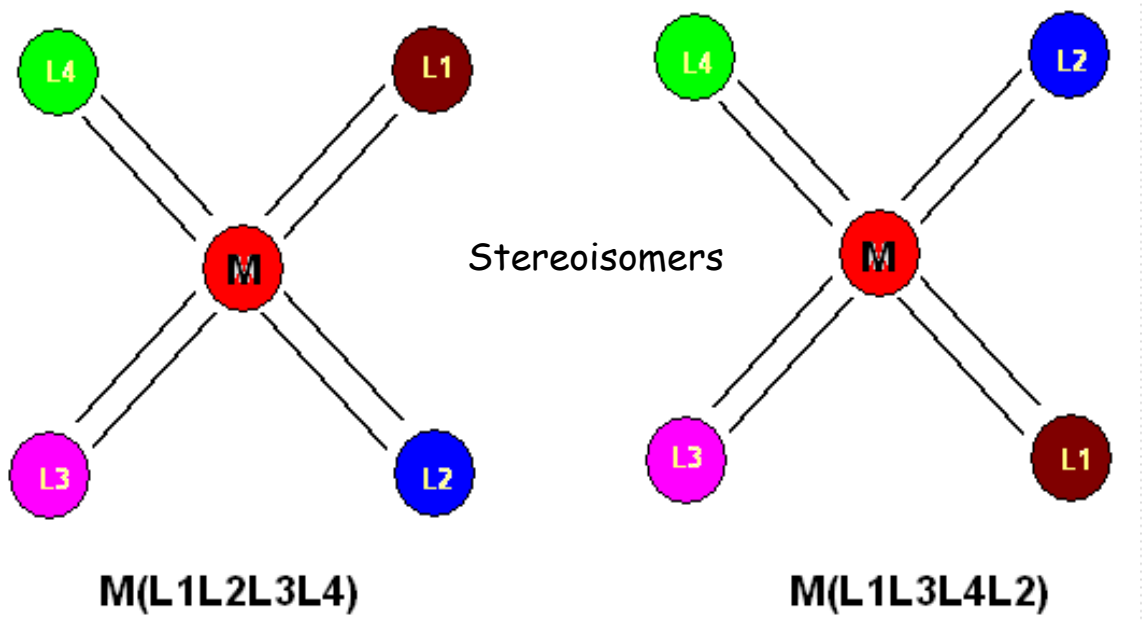
C-C-O bond sequence C-O-C bond sequence

Isomers: The compounds having same molecular formula but different arrangement of their atoms in space are called isomers of each other.

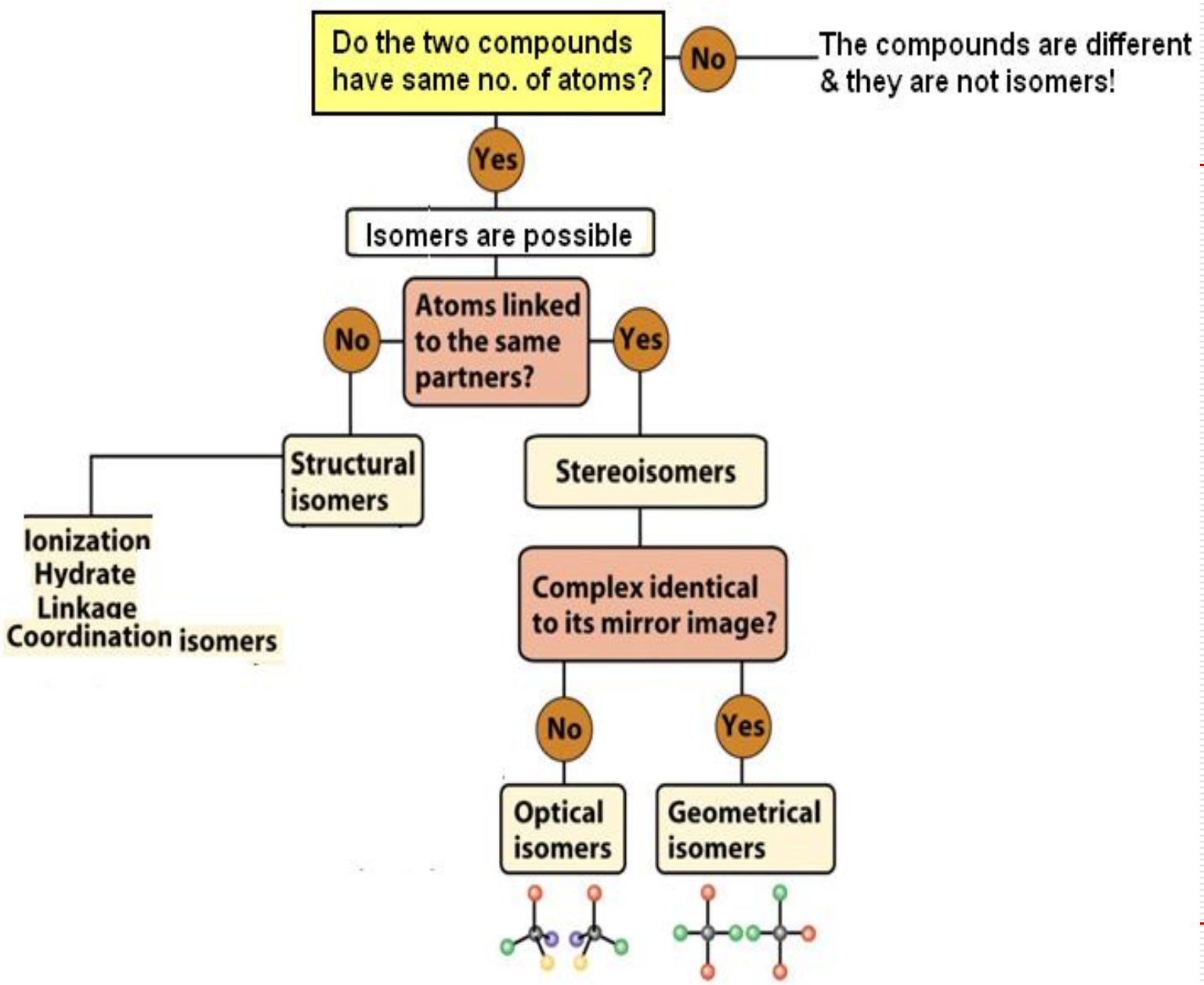
CH_3CH_2OH and CH_3OCH_3

Ethyl Alcohol Acetone

Stereoisomers: The compounds having same molecular formula, with the same central atoms linked to the same partners, differing only in their relative positions are called Stereoisomers



Isomerism


Do the two compounds have same no. of atoms?
No
The compounds are different & they are not isomers!
Yes
Isomers are possible
Atoms linked to the same partners?
No
Yes
Structural isomers
Stereoisomers
Ionization
Hydrate
Linkage
Coordination isomers
Complex identical to its mirror image?
No
Yes
Optical isomers
Geometrical isomers

Types of Stereoisomers

Two types;

a)Geometrical: Cis (Z)and Trans(E)

b)Optical: d (+) or l (-)

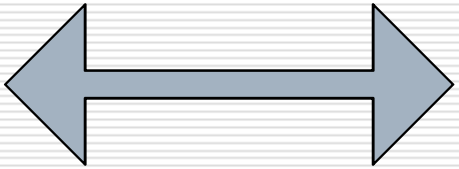
c)Structural

d) Coordination position

Geometrical isomers

Cis: (or Z- Zusammen means Togather): If two atoms (or molecule) attached to the same central atoms (metal) are on the *same side* (within 90 degree), it is called *Cis isomer*.

Trans: (or E- Entagenen means Opposite): If they are *far apart* (at 180 degree) it is called *trans isomer.*

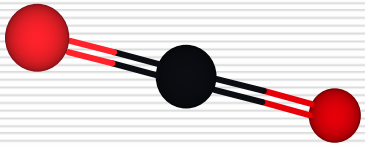


Geometrical isomers:

C.N : 2: *Linear Geometry:*

ligands are only180 degree apart !

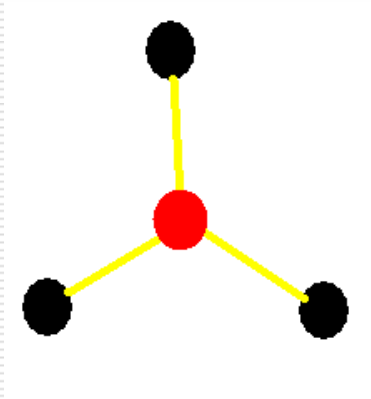
Means only TRANS isomer No CIS



C.N : 3: *Triangular Geometry:*

ligands are at 120 degree apart !

Means we cannot decide whether it is CIS/TRANS

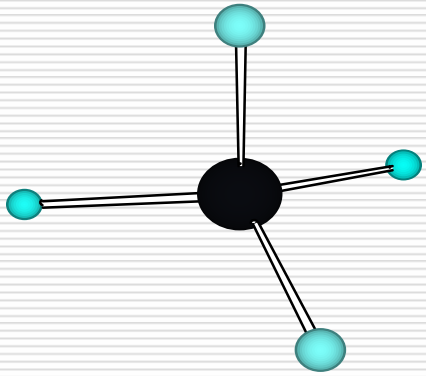


Geometrical isomers in CN 4:

For C.N. =4: Two structures possible

a) Tetrahedral: No isomerism

(since all groups are at tetrahedral angle from each other (i.e. 108.27')

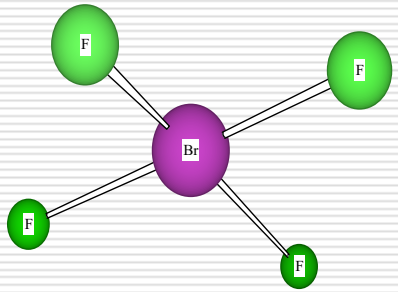


Angle: 108.5 degree

NOT EXACTLY 90 NOR 180,i.e.MIDDLE! Therefore cannot decide whether it is Cis or Trans!

b) Square planar: Shows isomerism

(since all groups are at 90 degree so two same group can be placed at 90 Or 180 degree)



Angle: 90/180 degree

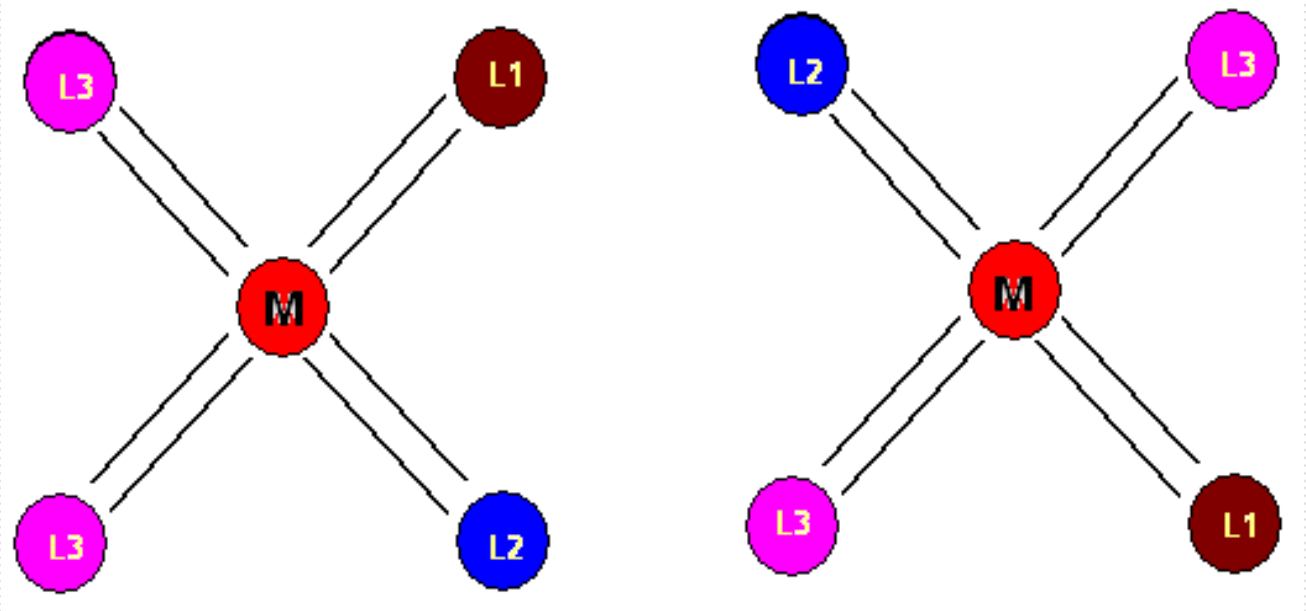
Geometrical isomers in Square Planar: (CN = 4)

Examples:

1. Ma_2bc

or Mab_2c

or $Mabc_2$ [where, M=Pt, a= NH_3, b= Py, c=H_2O]

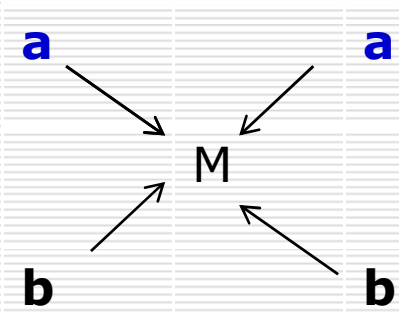


L_3 within 90:CIS **L_3 within 180:TRANS**

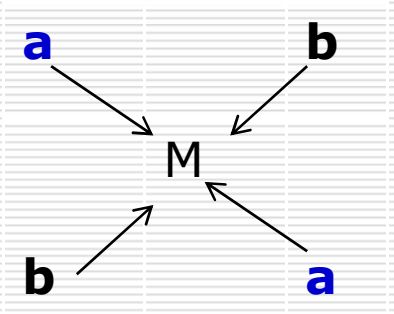
Geometrical isomers in Square Planar: (CN = 4)

Examples

2. Ma_2b_2 **[e.g.M= Pt, Pd,A=Cl,Br,I , B=NH_3, Py]**



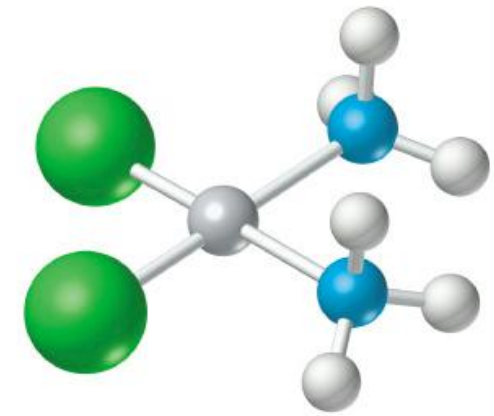
Cis: Ma_2b_2



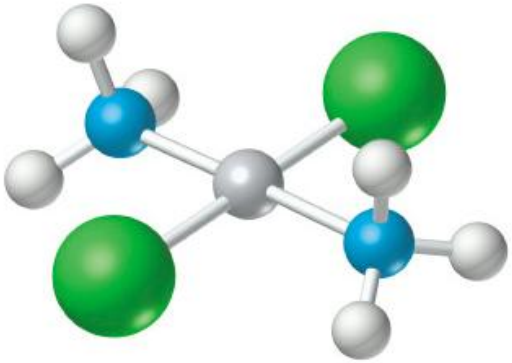
Trans:Ma_2b_2

Geometric Isomerism

Ma_2b_2



cis-$[PtCl_2(NH_3)_2]$



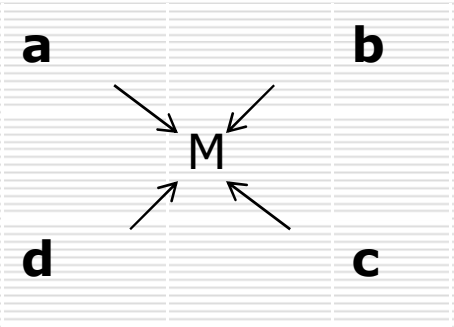
trans-$[PtCl_2(NH_3)_2]$

Geometrical isomers in Square Planar: (CN = 4)

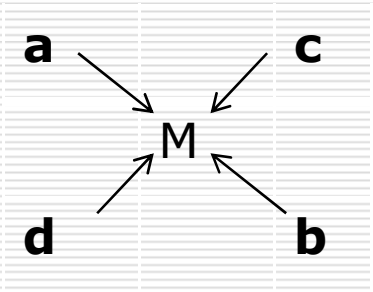
Examples

3.Mabcd **[e.g. M =Pt,a= Py, b= NH_3,c=Cl, d=Br]**

In such example, we have to consider any 2 ligand same (e.g. a & c same)

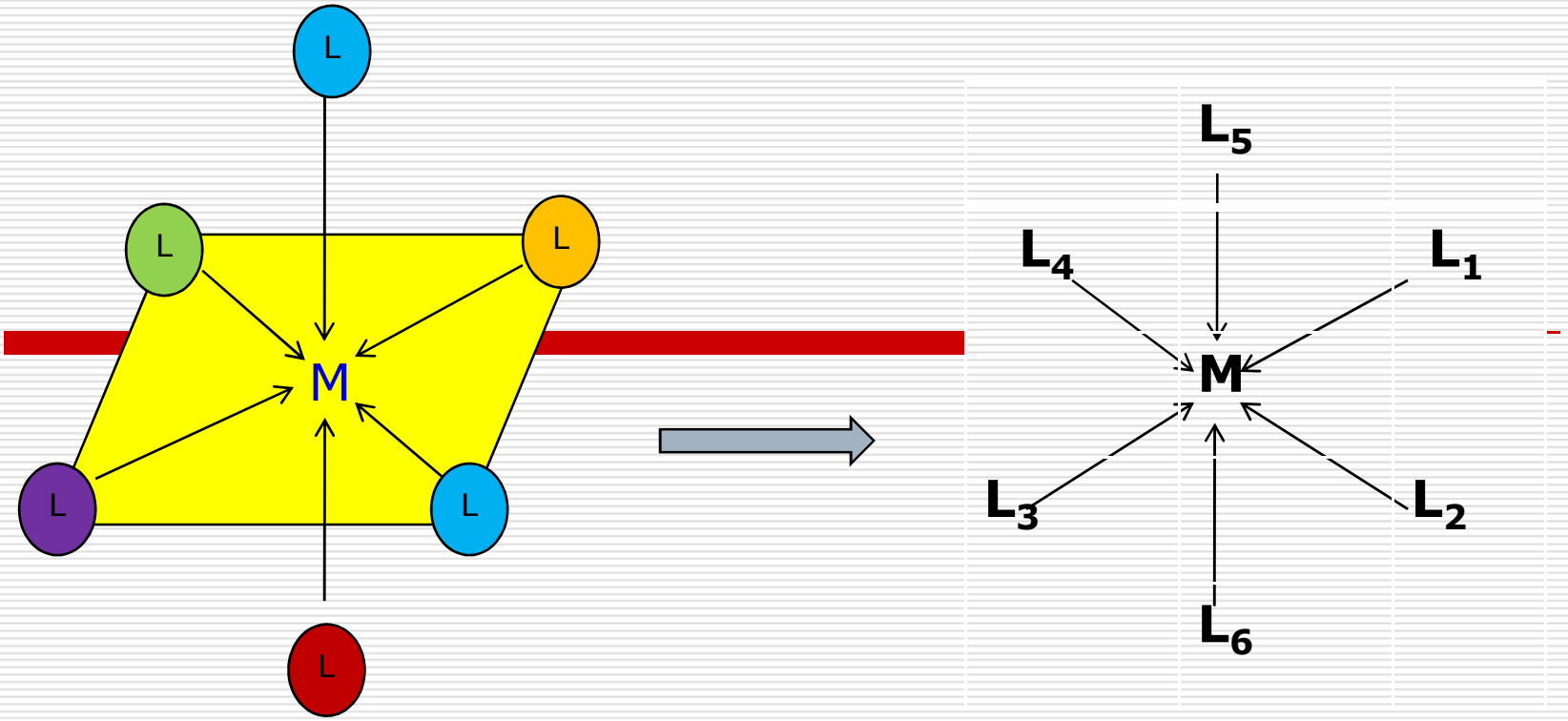


Cis:



Trans:

Geometrical isomers in Octahedral (CN = 6)



Octaherdal:

CIS:(1,2),(2,3),(3,4),(1,4),(1,5),(2,5),(3,5),(4,5),(1,6), (2,6),(3,6),(4,6).

TRANS: (1,3),(2,4) & (5,6)

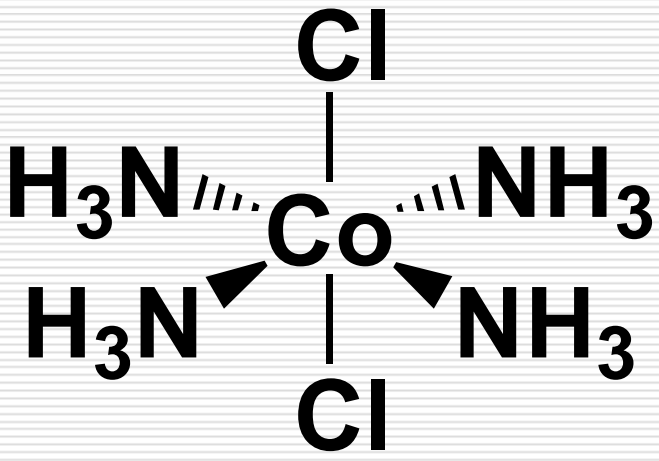
Geometrical isomers in Octahedral: (CN = 6)

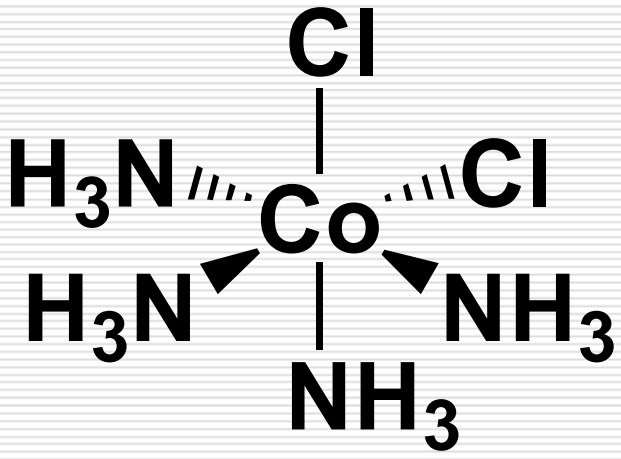
Examples:

1. Ma_6	No isomer, Single isomer!
2. Ma_5b	No isomer, Single isomer!
3. Ma_4b_2 OR a_2b_4	2 isomers
4. $Ma_2b_2c_2$	2 isomers
5. Ma_3b_3	Facial& Meridial
6. Mabcdef	2 isomers

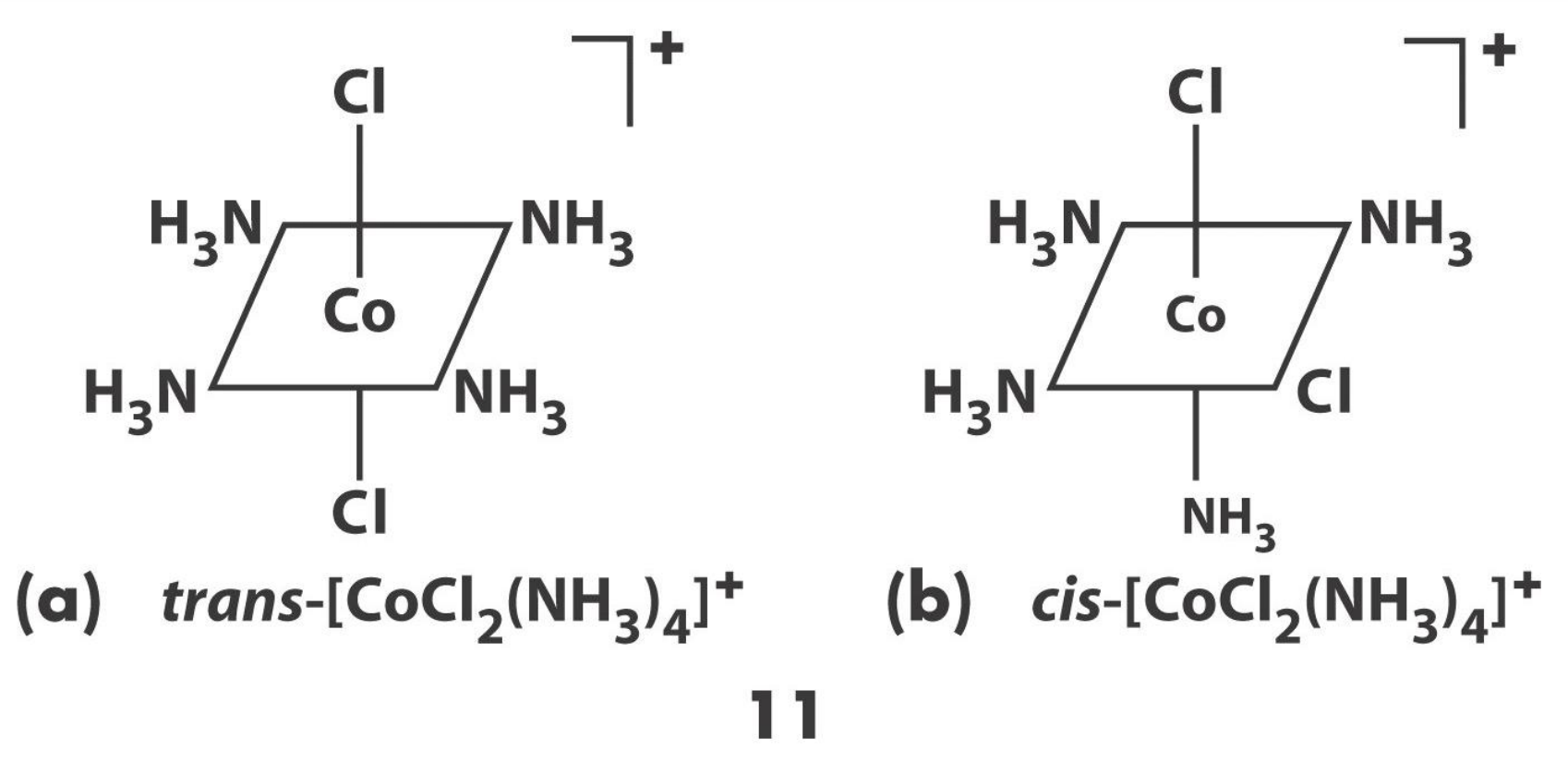
Stereoisomers: geometric isomers (cis and trans)

Example: Ma_4b_2 or Ma_2b_4



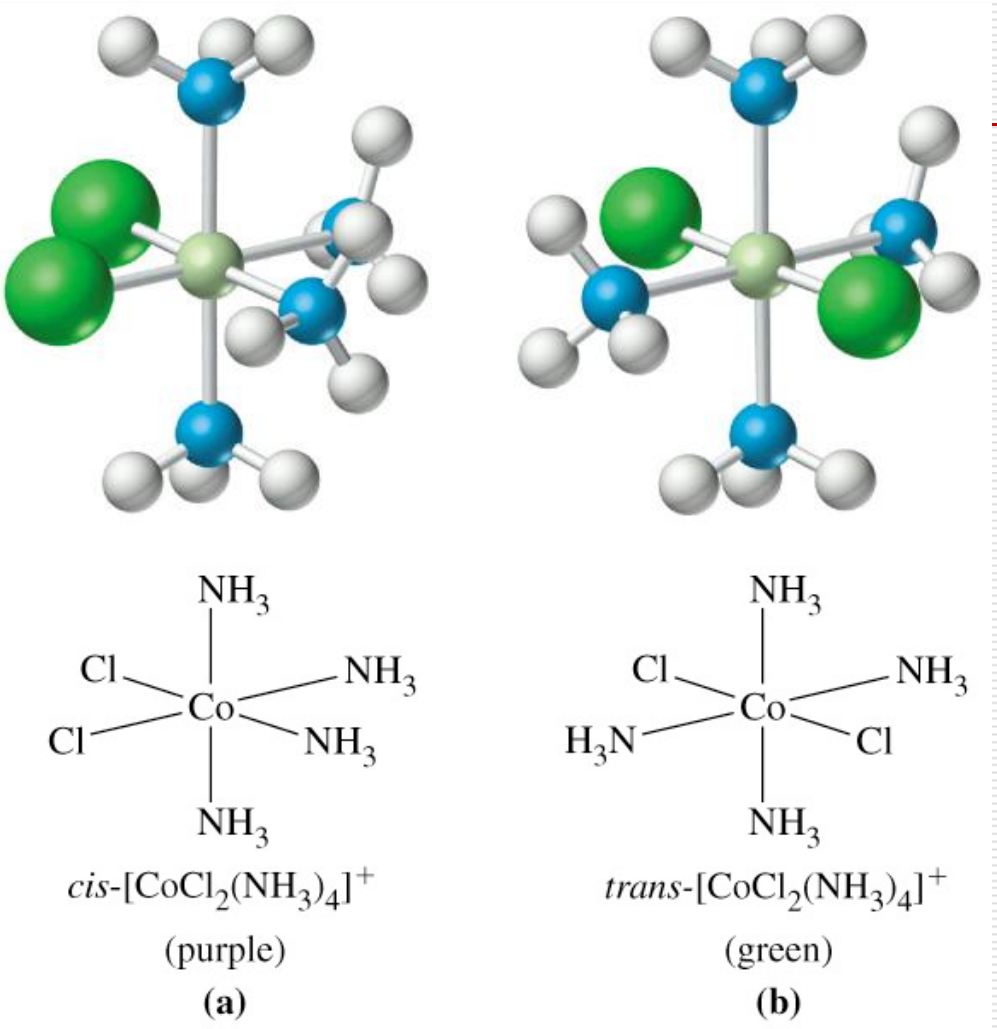


Stereoisomers: geometric isomers (cis and trans)



11

Geometric Isomerism

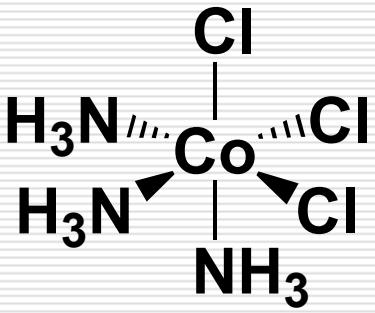


facial & meridian isomers

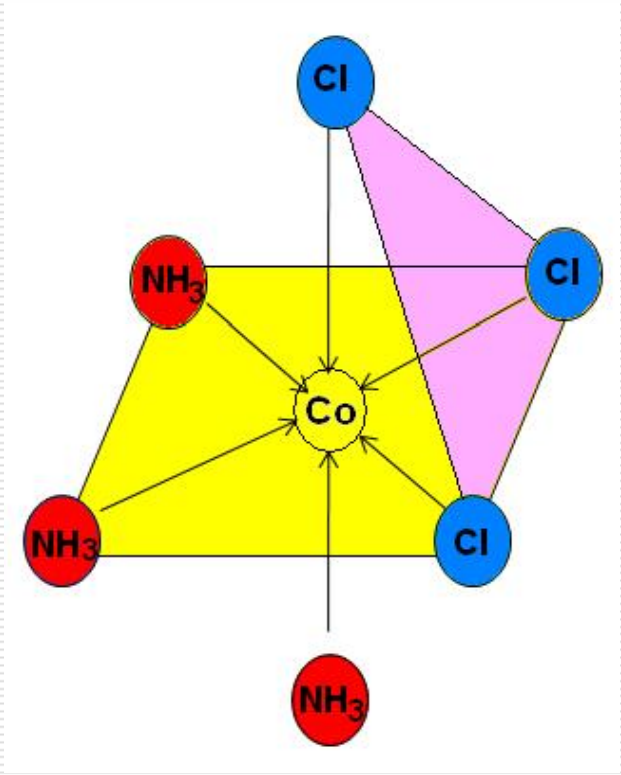
FACIAL: Same ligands are adjacent (on triangular face)

Ma_3b_3

facial (fac)

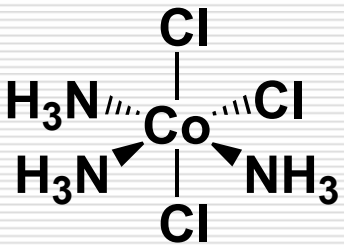


3 Cl^- (and 3 NH_3) ligands are adjacent (on triangular face)

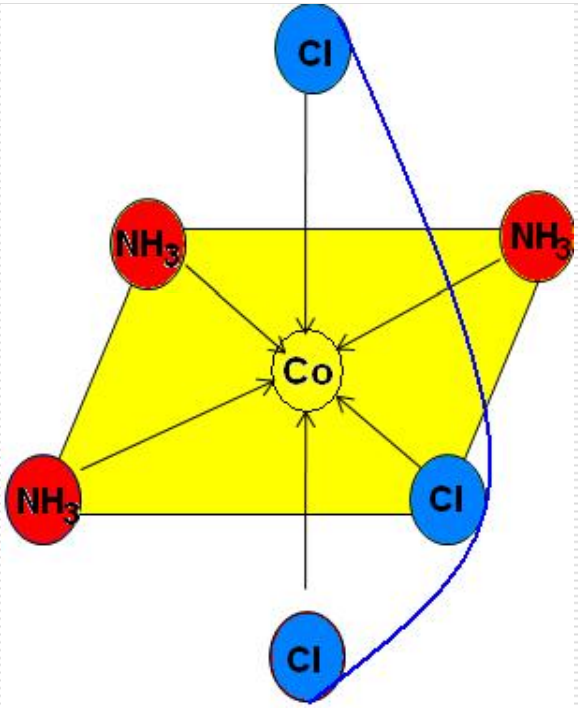


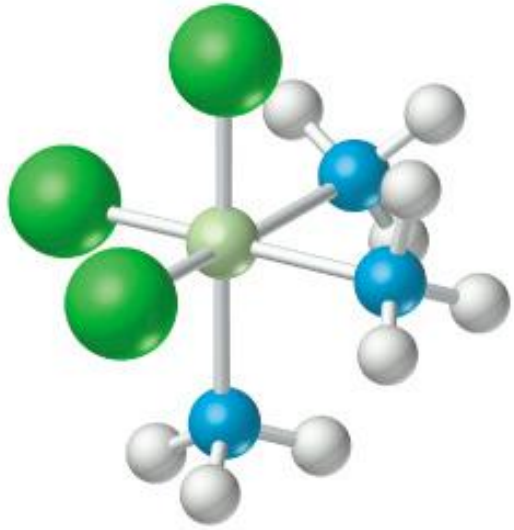
MERIDIAN: Same ligands can be joined to the ion constituting half of perimeter.

Ma_3b_3 meridian (mer)

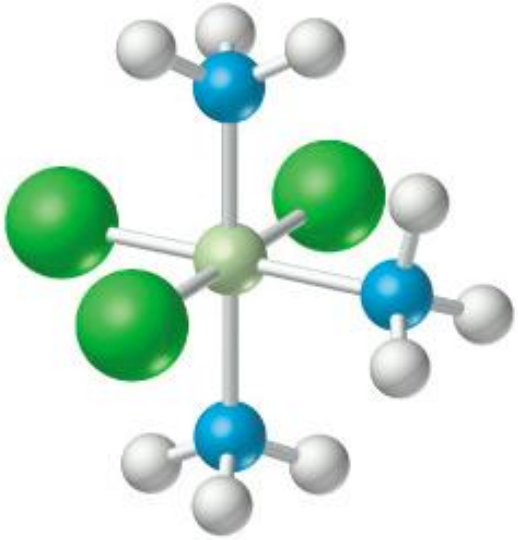


3 NH_3 ligands in one plane, 3 Cl ligands in a perpendicular plane



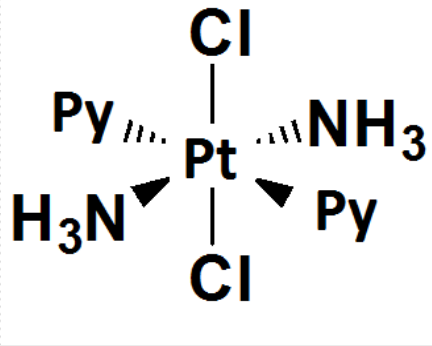


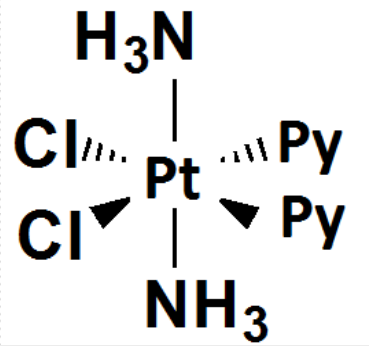
fac-$[CoCl_3(NH_3)_3]$

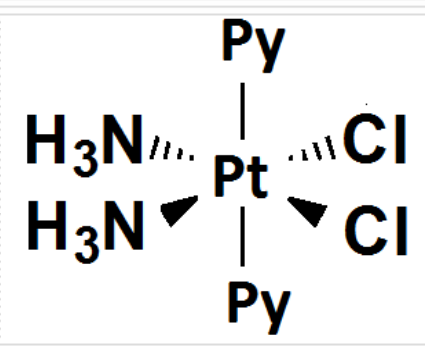


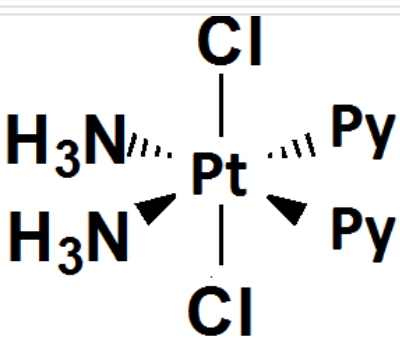
mer-$[CoCl_3(NH_3)_3]$

$Ma_2b_2c_2$

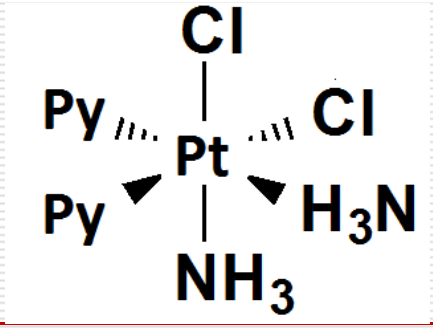








Trans



Cis

Optical Isomers (Enantiomers)

Two isomers are mirror images which are **not** superimposable. (called Enantiomers)

Any molecule which possesses a plane of symmetry is superimposable on its mirror image.

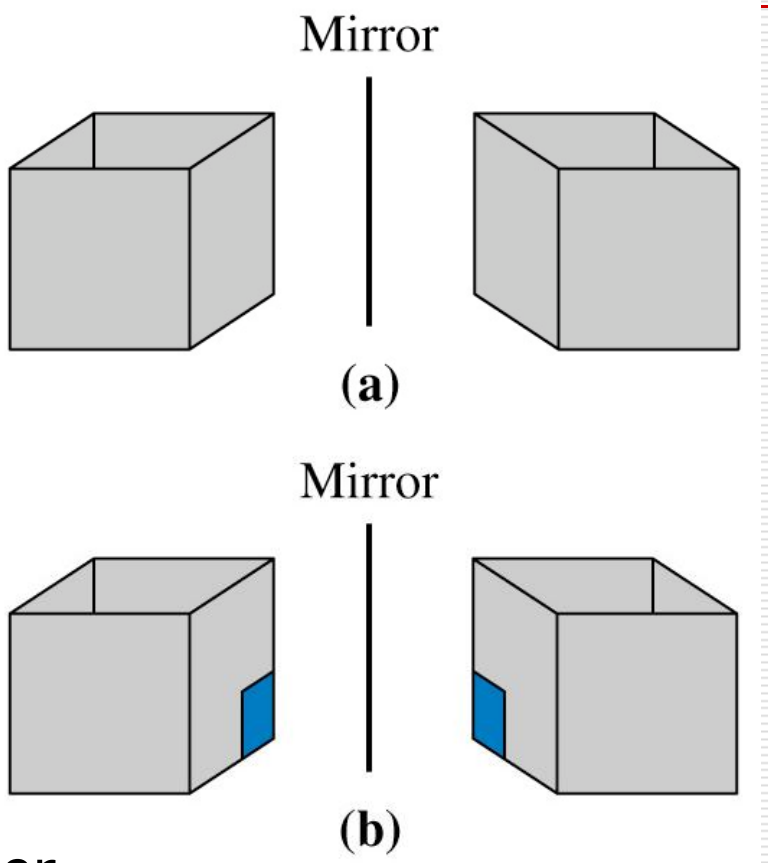
Molecules having achiral (asymmetric) centers are optically active.

Two isomers showing opposite optical activity are called optical isomers.

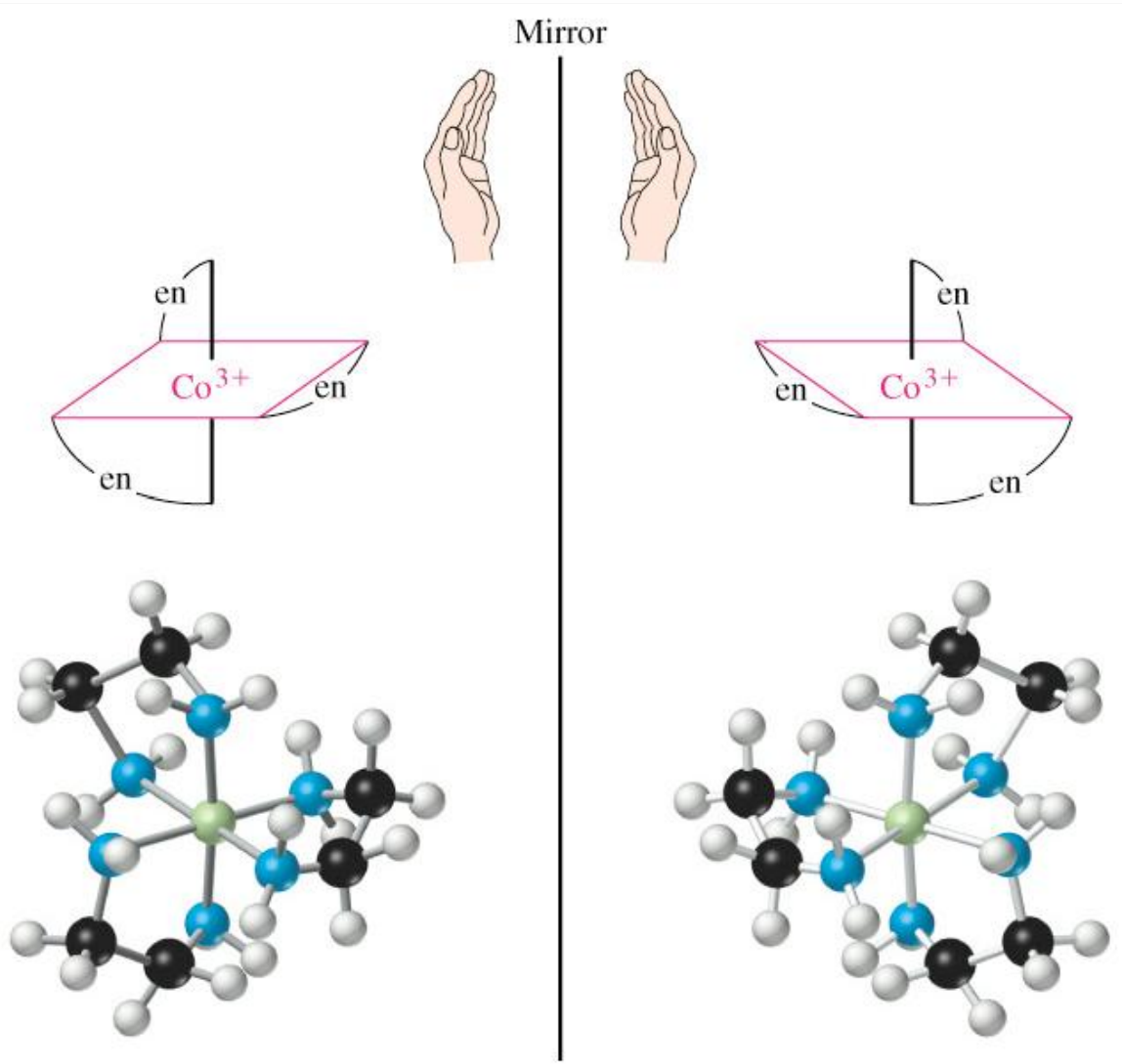
Enantiomers do not have a plane of symmetry.

Enantiomers rotate polarized light in different directions; therefore, enanotiomers are also termed "optical isomers"

Mirror images & nonsuperimposability



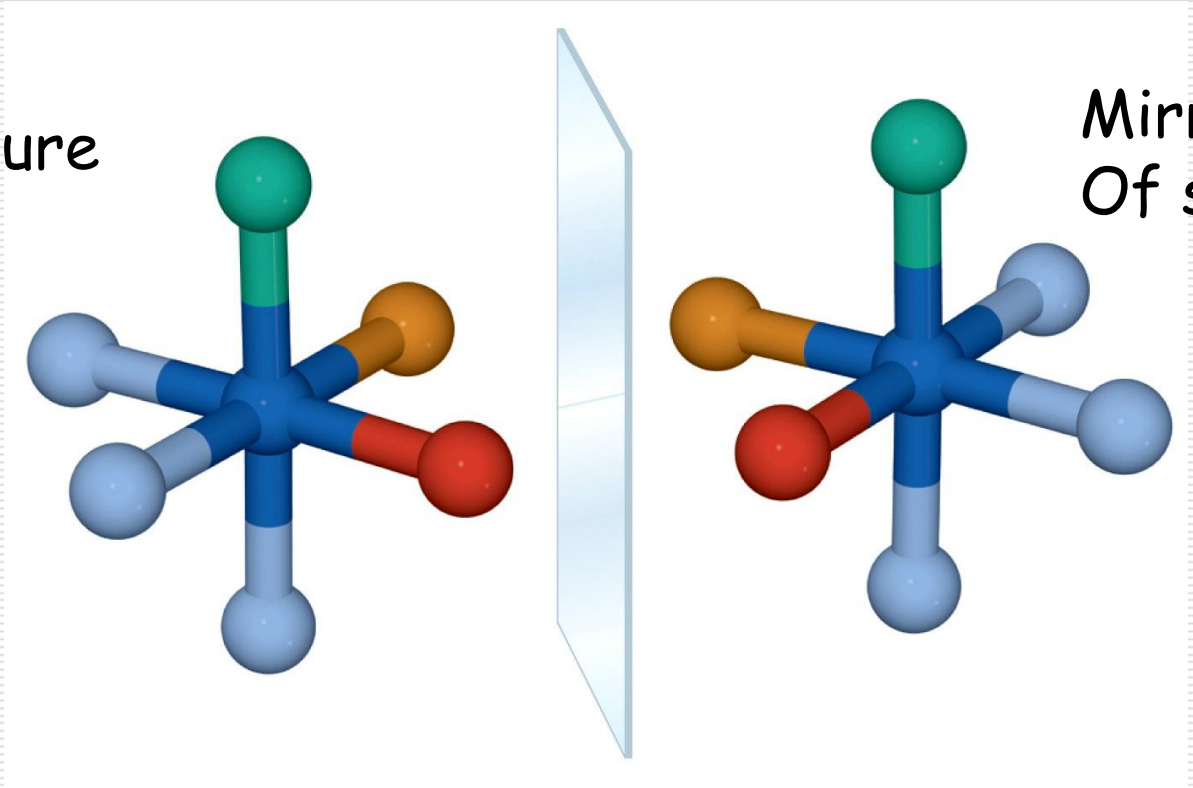
One image over other
a) match (superimposable)
b)do not match (nonsuperimposable)


Mirror
en
en
en
Co^{3+}
en
en
en
en
Co^{3+}

Meaning of "Achiral"

A structure is termed ***achiral*** if it is not superimposable on its mirror image

Structure



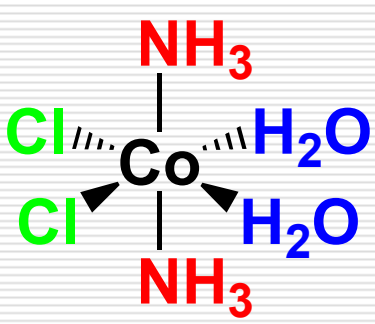
Mirror image
Of structure

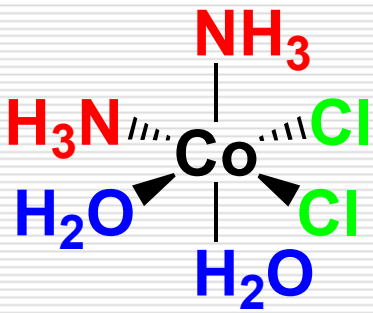
Two achiral structures: ***non superimposable mirror images therefore are Enantiomers!***

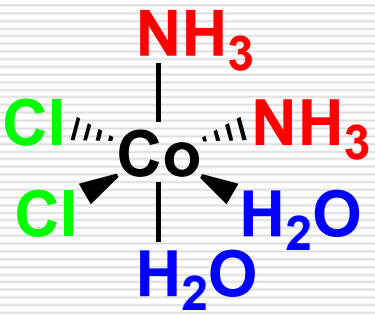
plane of symmetry: Enantiomers are possible

A molecule possessing a plane of symmetry is chiral and is superimposible on its mirror image. Enantiomers are NOT possible.

Are the following chiral or achiral structures?



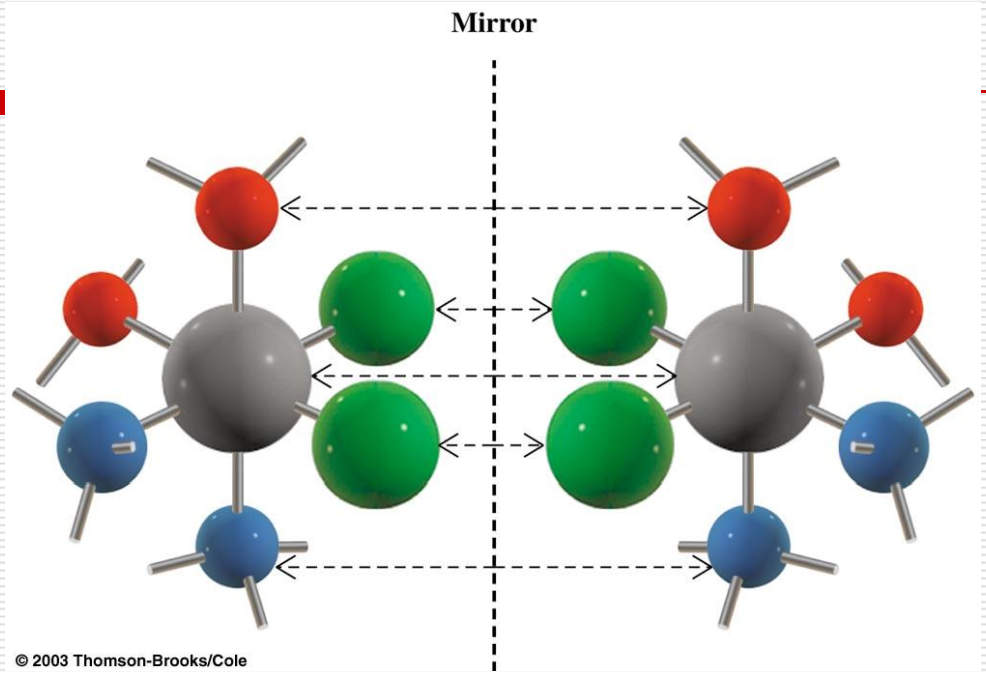


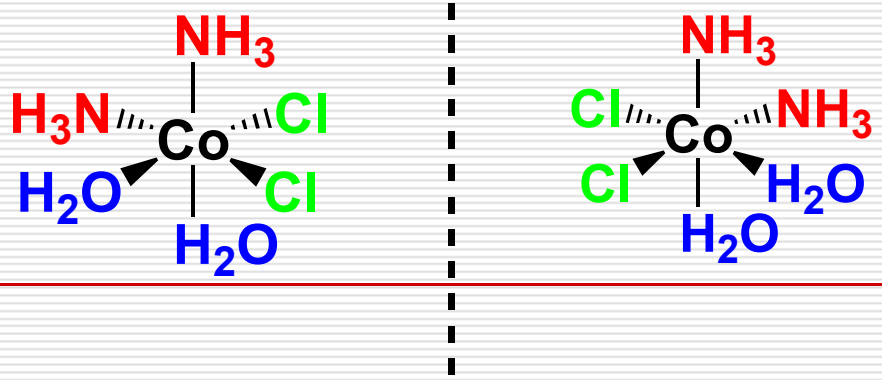


Plane of symmetry
chiral (one structure)

No plane of symmetry
Achiral (two enantiomer)

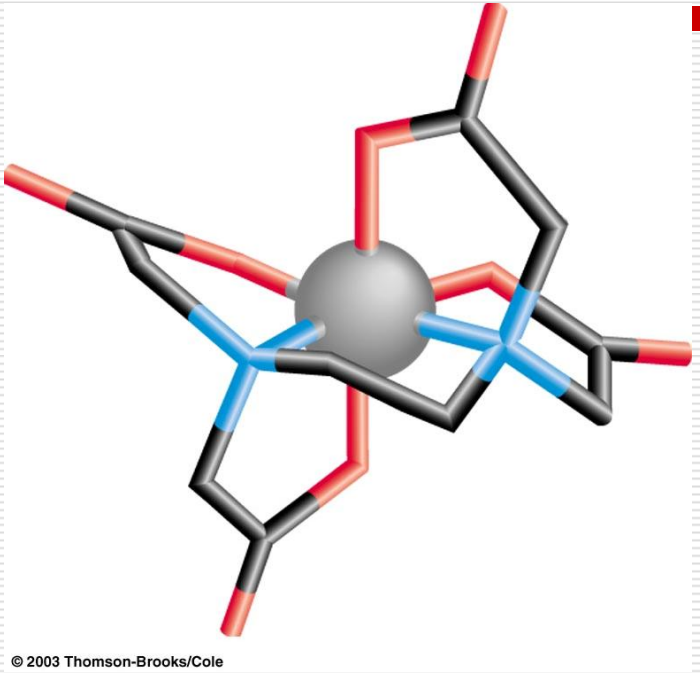
Two coordination complexes which are enantiomers

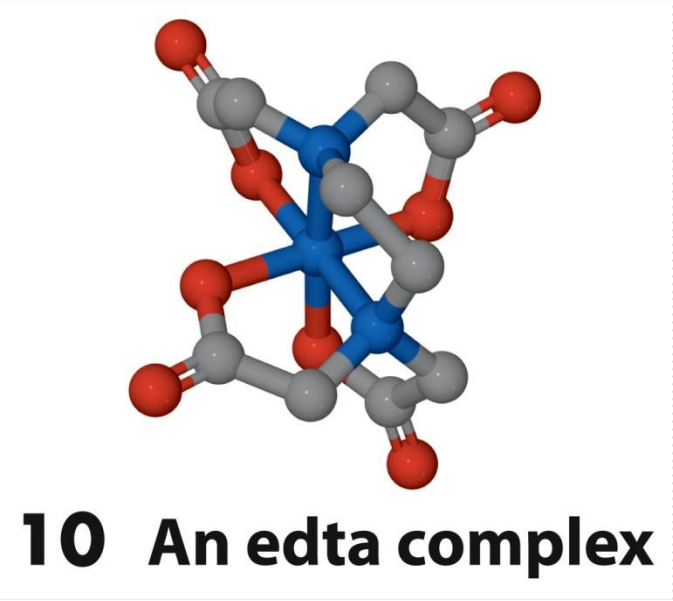




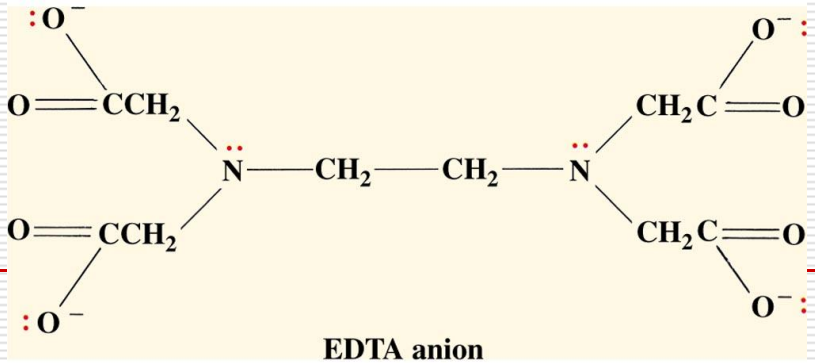
EDTA complexes are optically active

No plane of symmetry





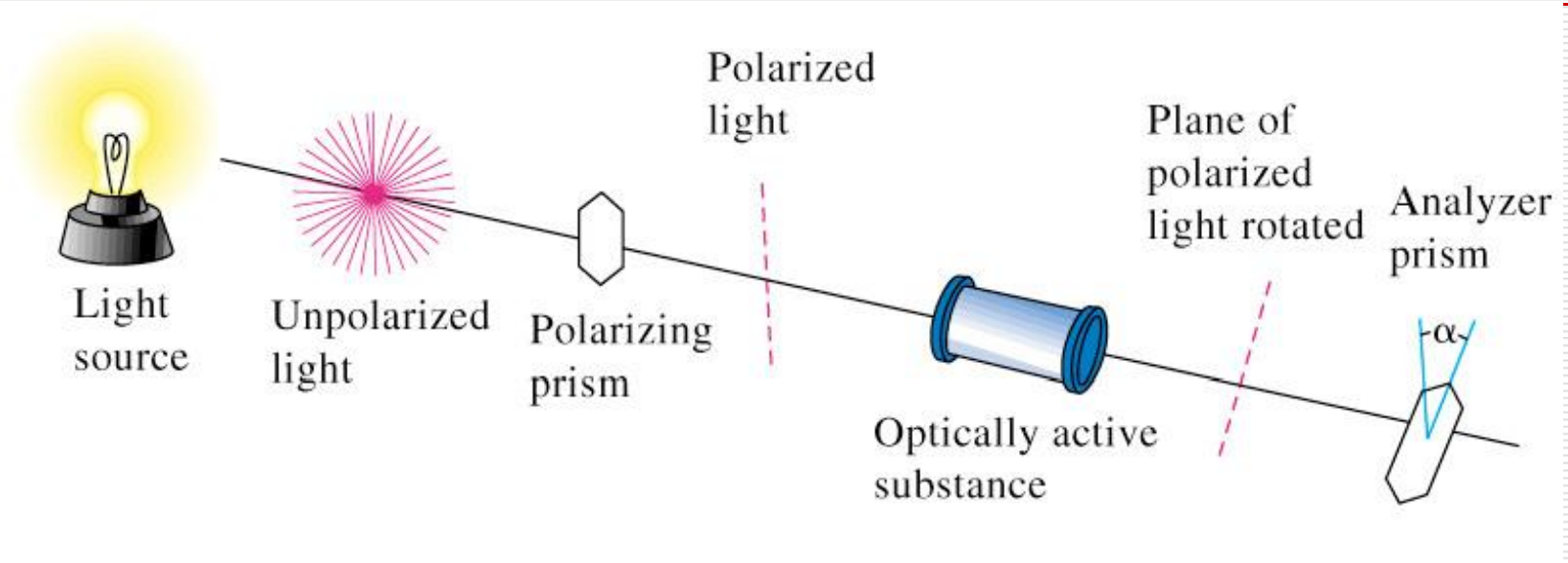
10 An edta complex



EDTA anion

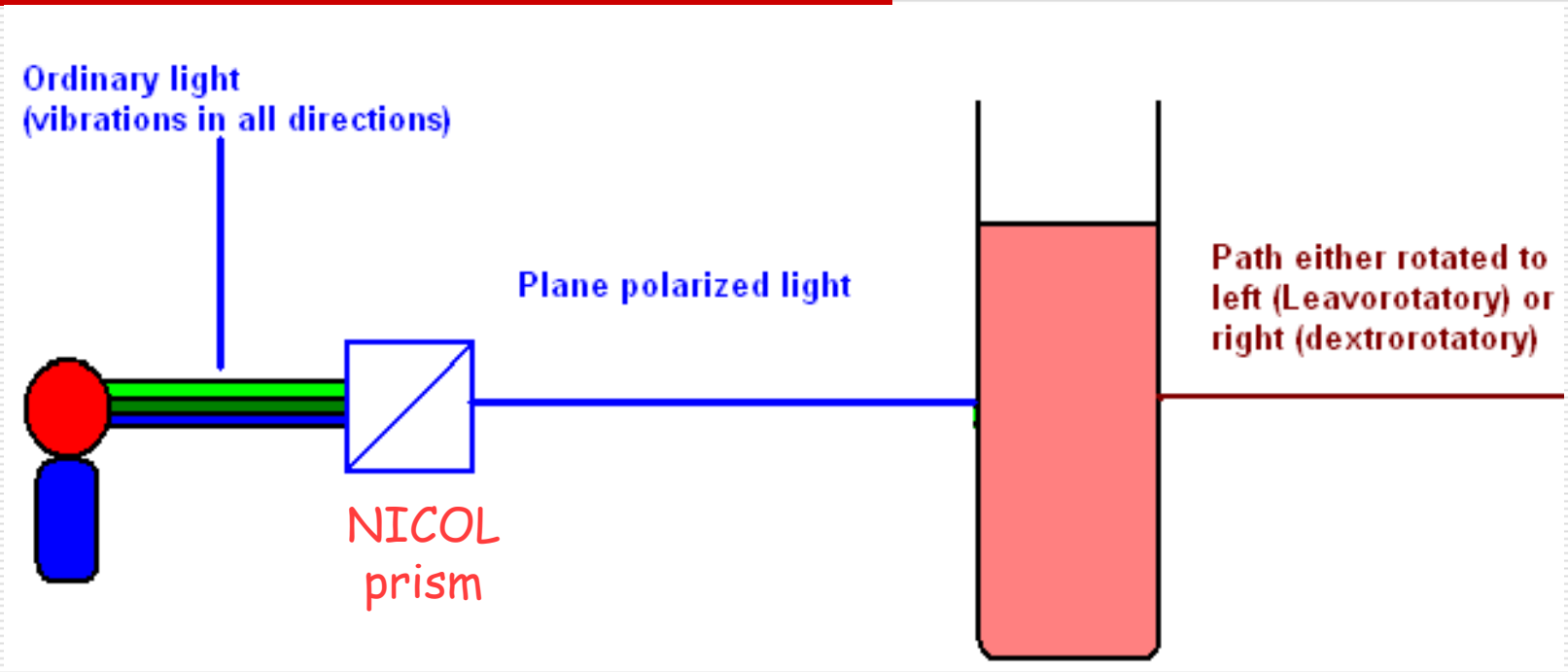
lhapur.

Optical Activity



dextrorotatory *d*-
levorotatory *l*-

Optical Activity



PPL: The light whose Vibrations are taking place in one plane.

The plane of this Vibrations is rotated either left or right

Optical Isomers: Square planer

M_{abcd}

No optical Isomerism

(Plane of Symmetry)

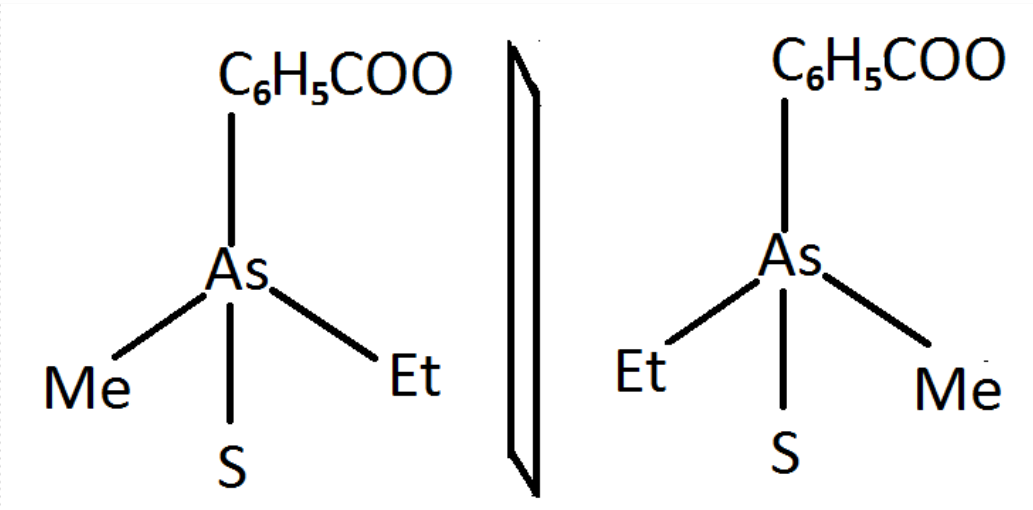
However complicated compound may show isomers
e.g. Iso butylene diammine meso stilbene diammine Pt(II)

$Pt(NH2.CH(C6H6).CH(C6H5).NH2)(NH2CH2.C(CH3)2.NH2]^{2+}$

Optical Isomers: Tetrahedral

M_{abcd}

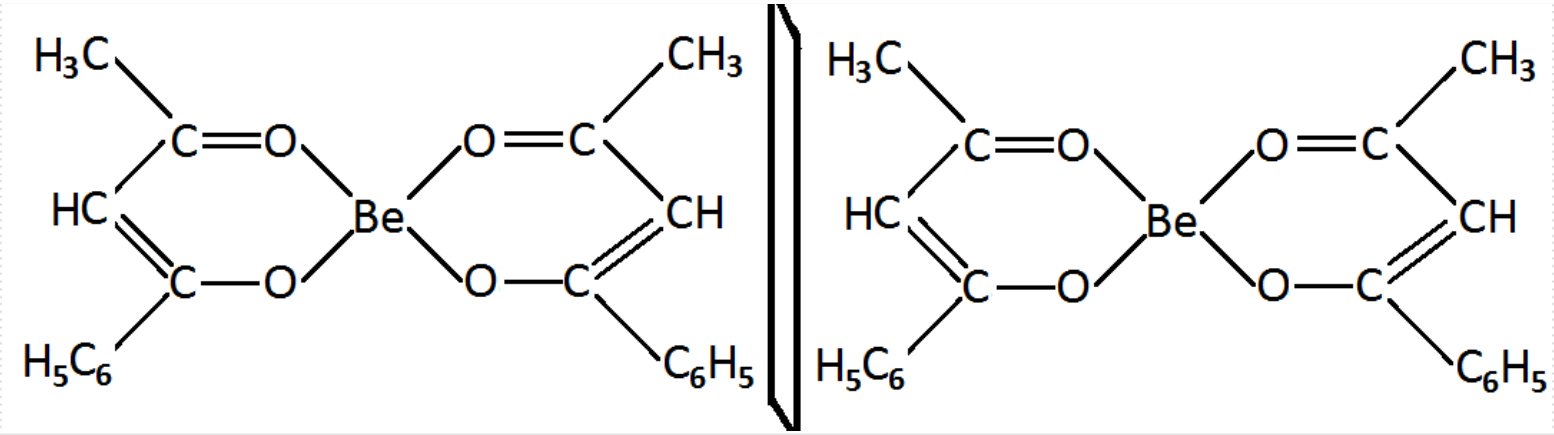
Can show optical Isomerism.



Optical Isomers: Tetrahedral

M_{abcd}

Can show optical Isomerism.

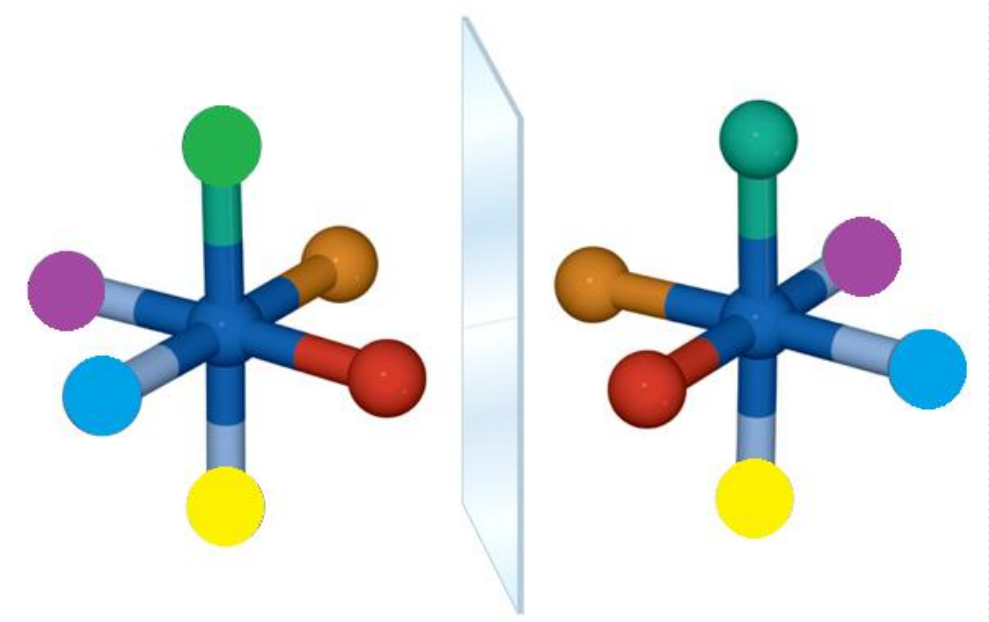


Bis benzoyl acetonato Be(II)

Optical Isomers: Octahedral

$M_{abcdefg}$

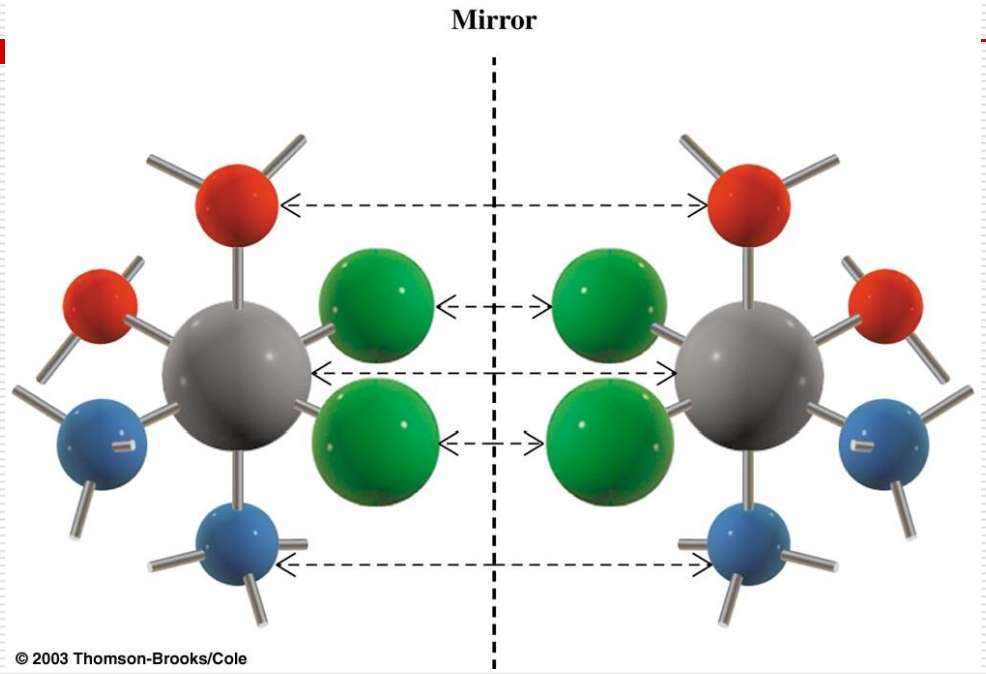
Can show optical Isomerism.

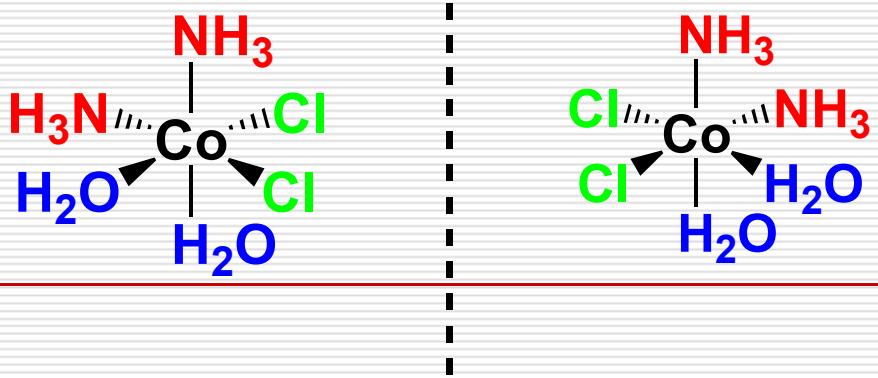


All different ligands attached to central metal ion can show isomerism. E.g $[Pt(Py)(NH_3)(NO_2)ClBrI]$ = 15 isomers!

Oh

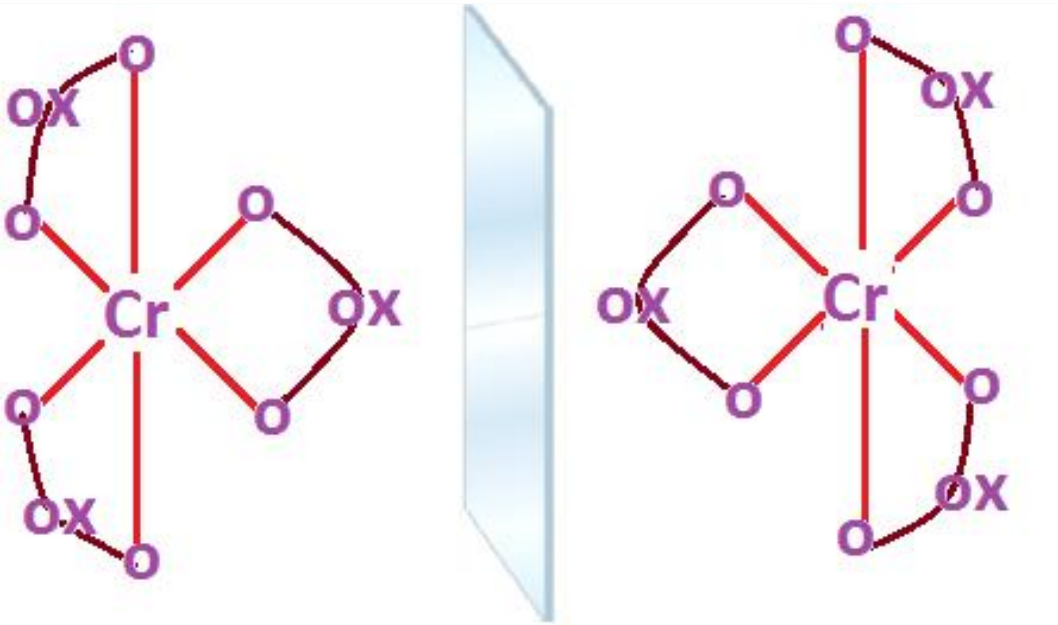
M_{a2b2c2}


Mirror
© 2003 Thomson-Brooks/Cole


NH3
H3N
Co
Cl
H2O
Cl
H2O
NH3
Cl
Co
NH3
Cl
H2O
H2O

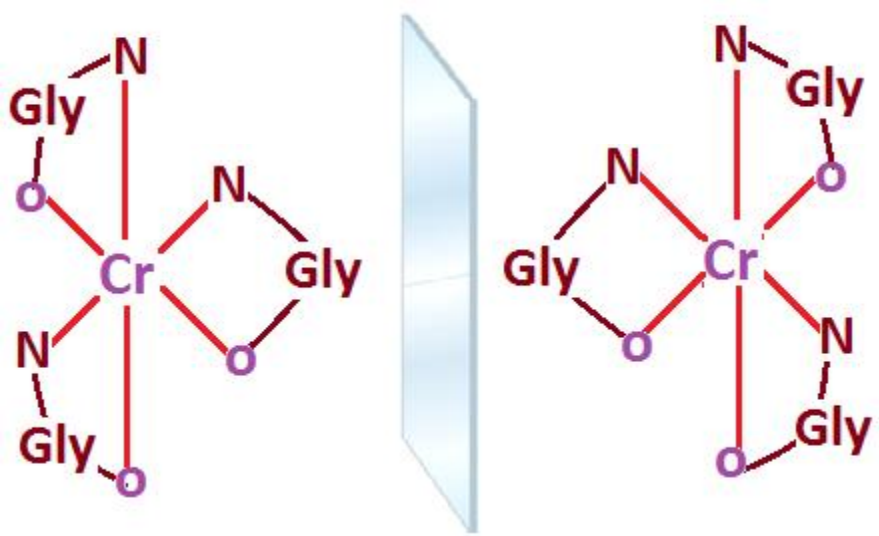
Complexes having bidentate ligands can show optical activity

$M(AA)_3$ type: e.g. 1. $[Cr(ox)_3]^{3-}$ 2. $[Co(en)_3]^{3+}$



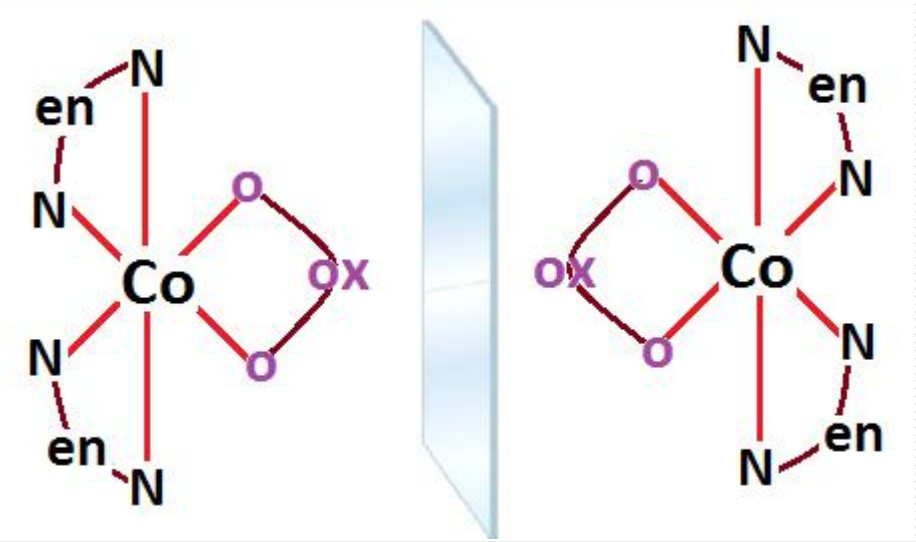
Complexes having bidentate ligands can show optical activity

$M(AB)_3$ type: e.g. $[Cr(gly)_3]^{3-}$



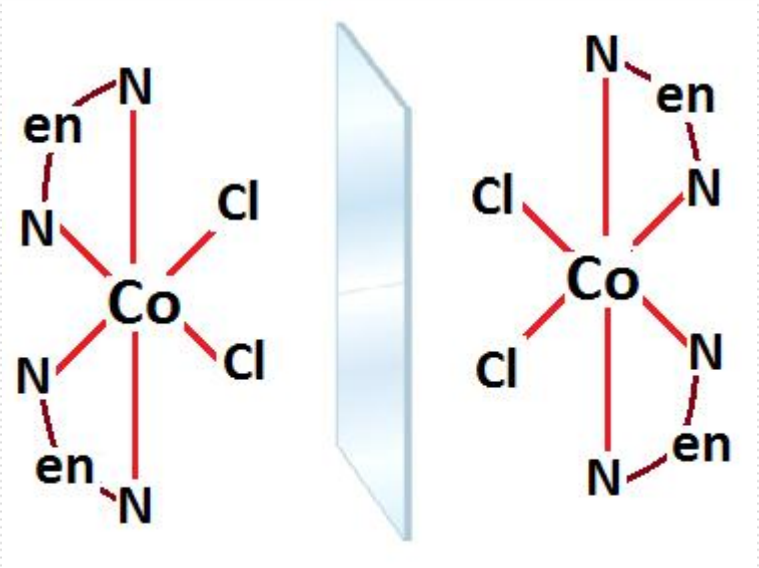
Complexes having bidentate ligands can show optical activity

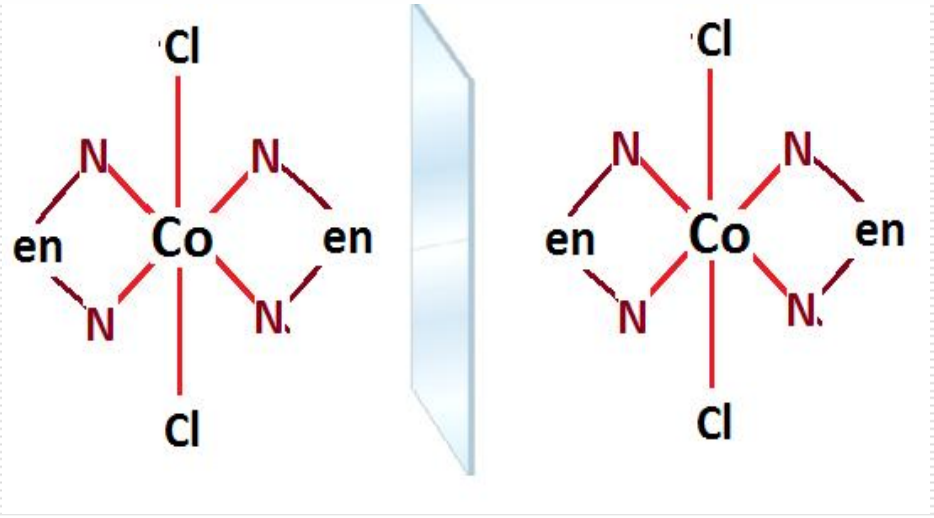
$M(AA)_2BB$ type: e.g. $[Co(en)_2(C_2O_4)]^+$



Complexes having bidentate ligands can show optical activity

$M(AA)_2a_2$ type: e.g. $[Co(en)_2Cl_2]^+$



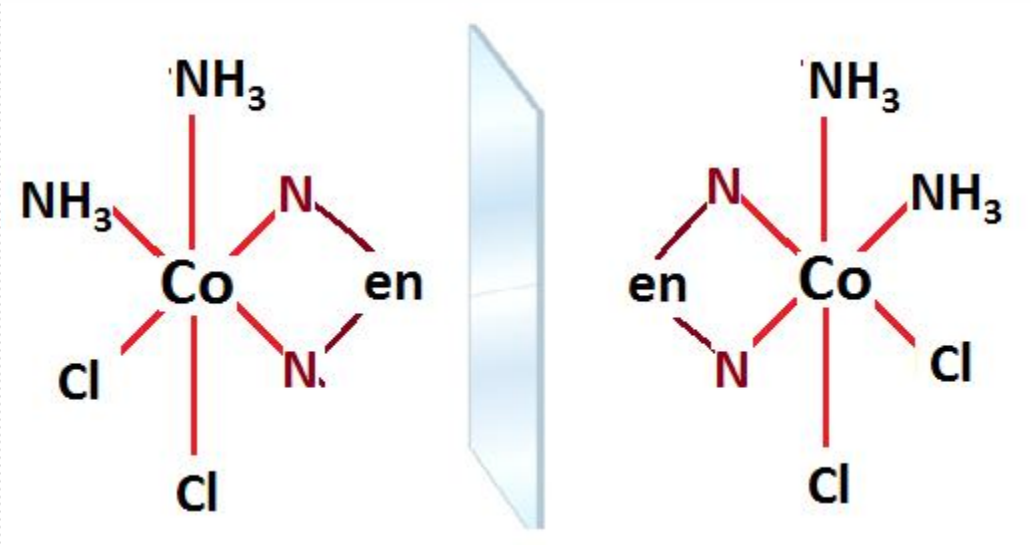


Cis: Optical active

Trans: Optical inactive

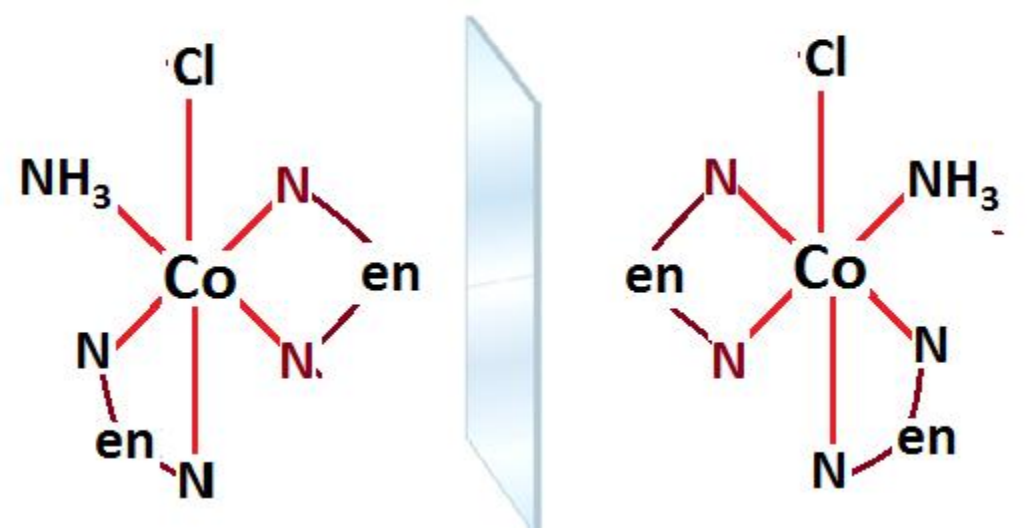
Complexes having bidentate ligands can show optical activity

$M(AA)_2ab$ type: e.g. $[Co(en)_2Cl_2(NH_3)_2]^+$



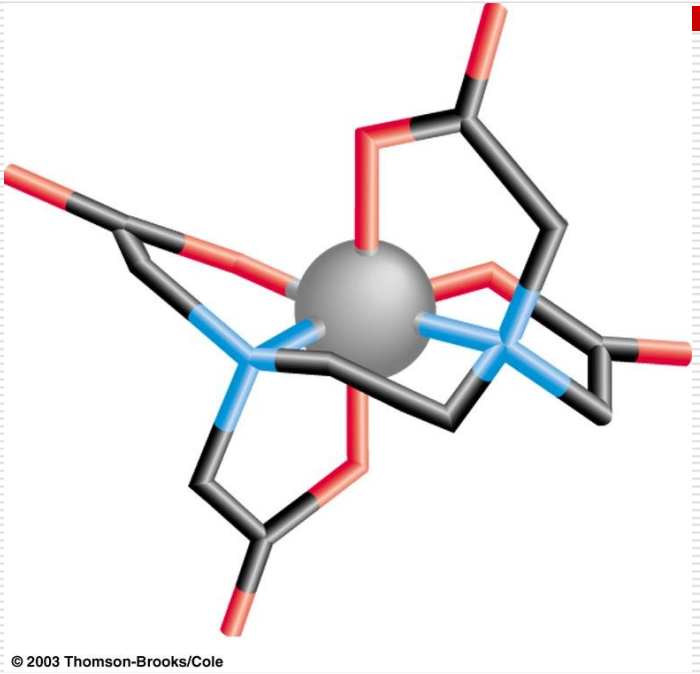
Complexes having bidentate ligands can show optical activity

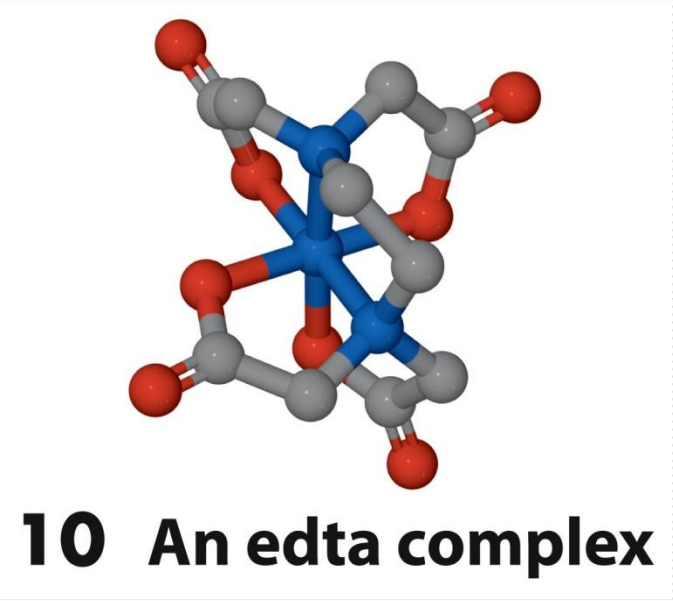
$M(AA)_2a_2b_2$ type: e.g. $[Co(en)_2ClNH_3]^{3-}$



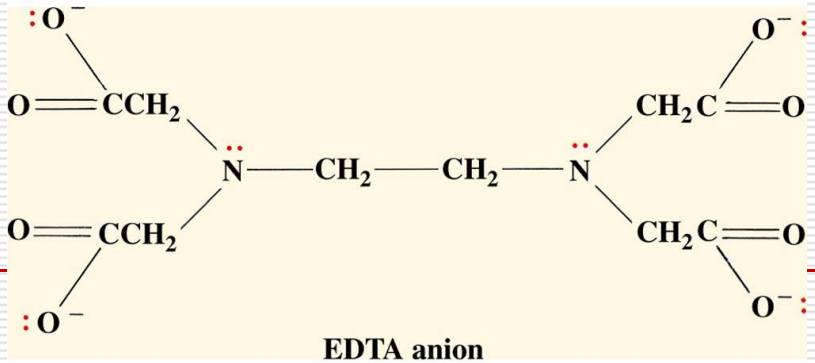
EDTA complexes are optically active

No plane of symmetry





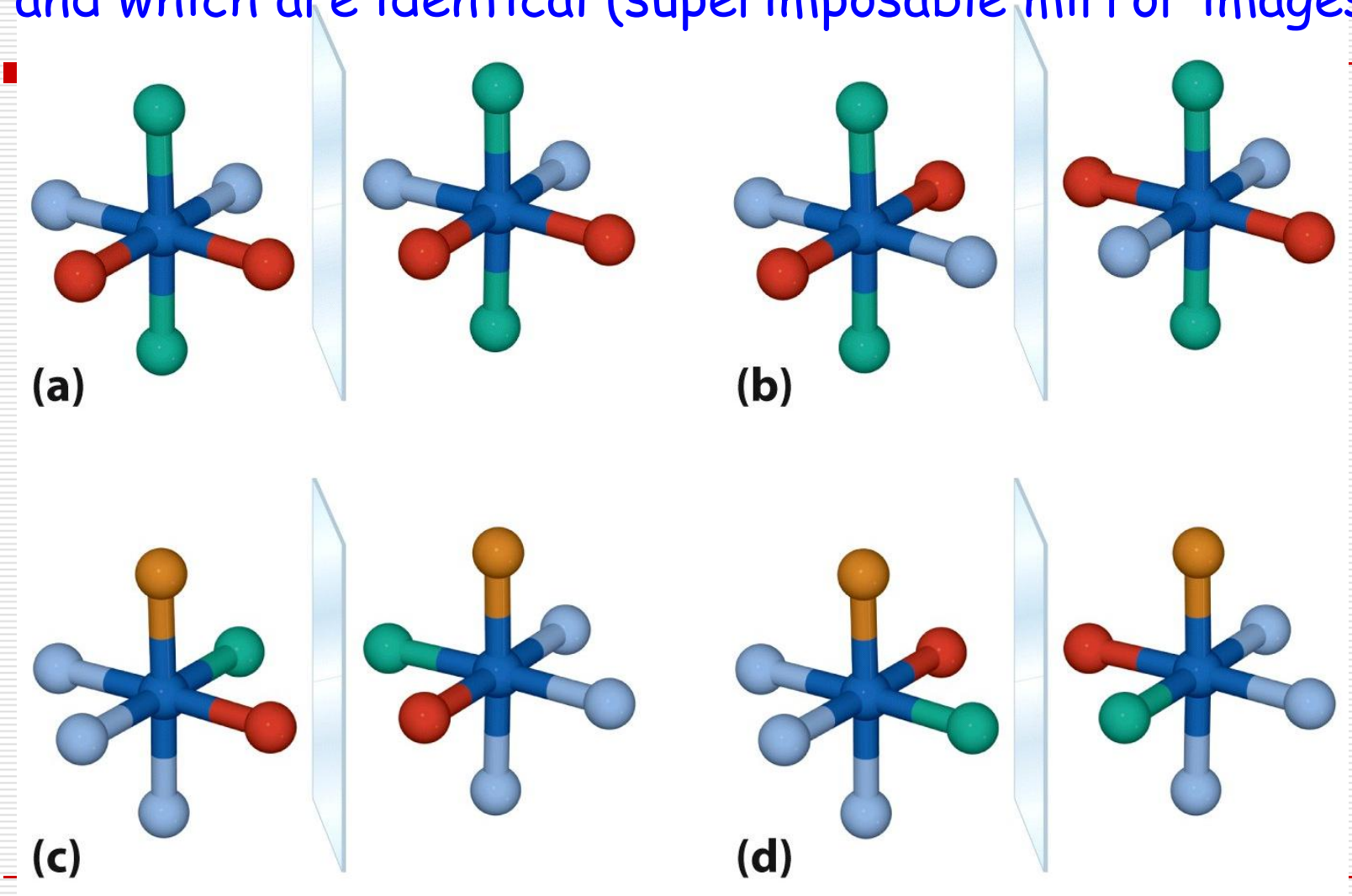
10 An edta complex



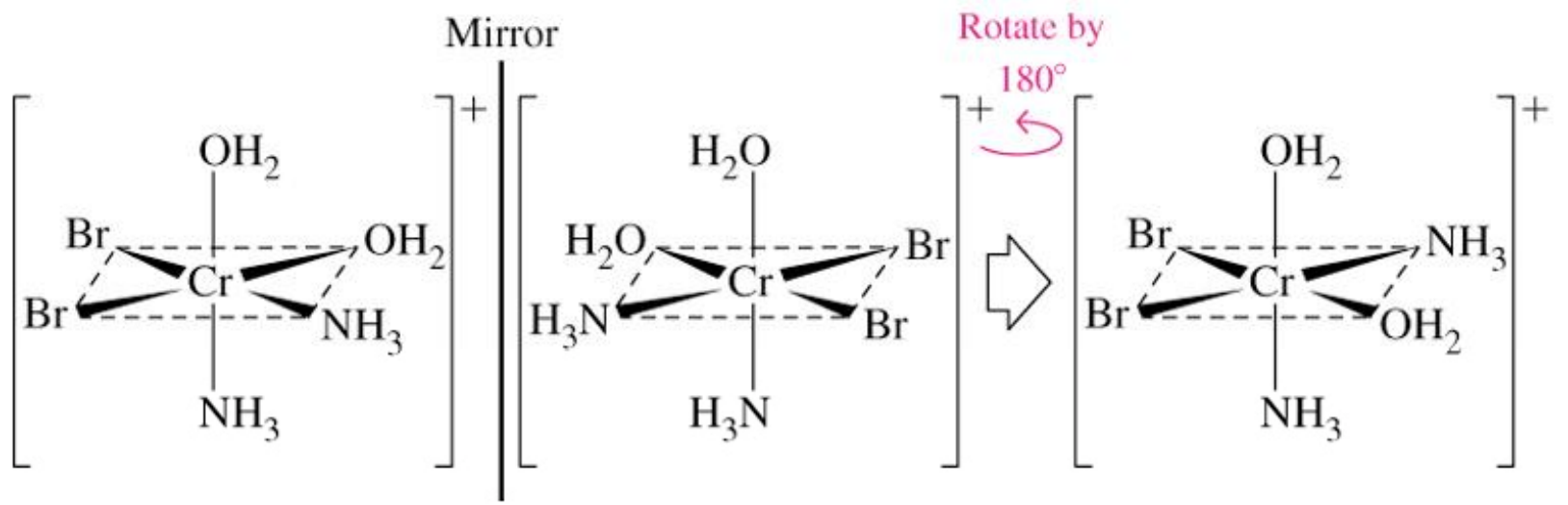
EDTA anion

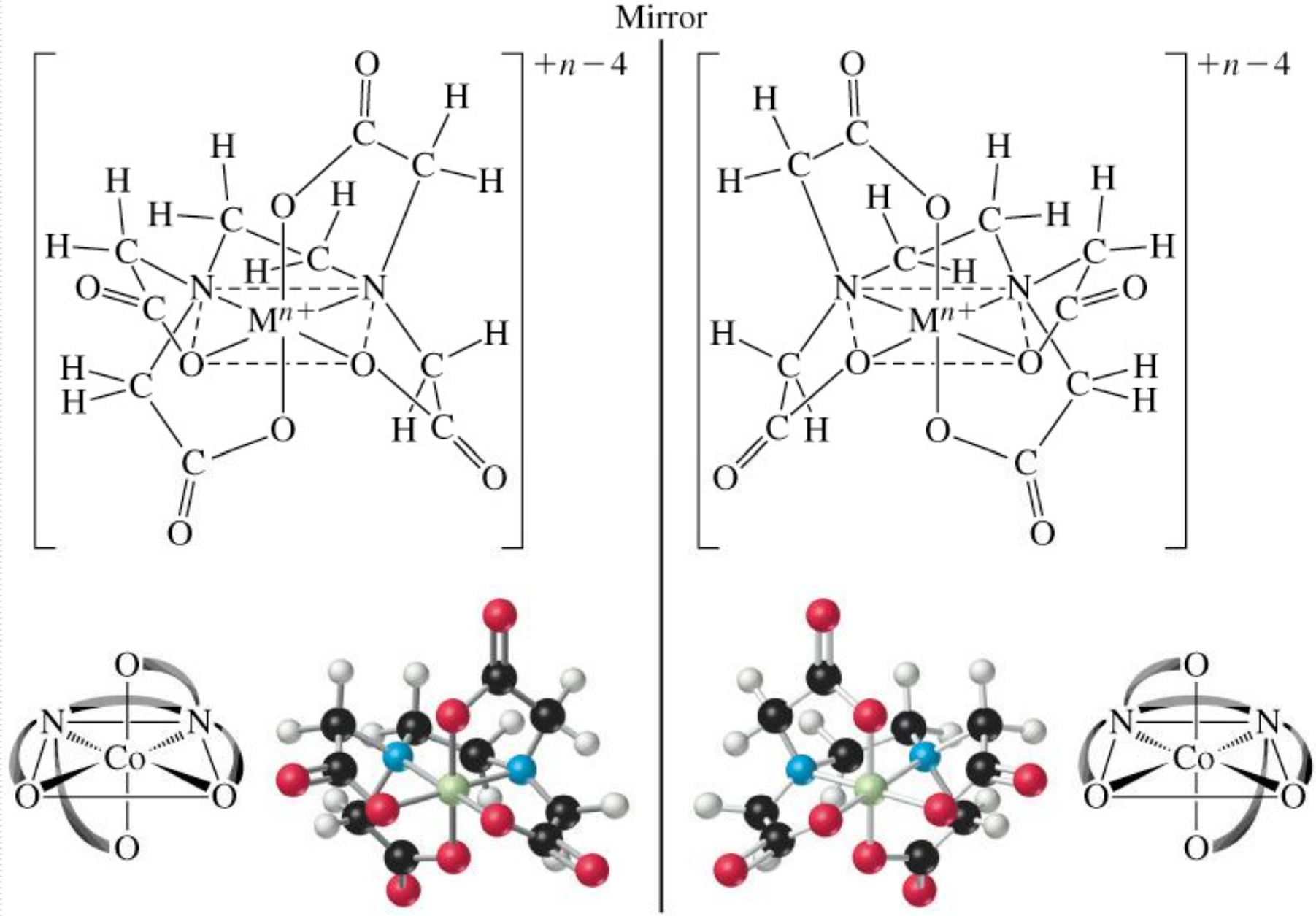
lhapur.

GUESS:
Which are enantiomers (non-superimposable mirror images) and which are identical (superimposable mirror images)?



Mirror Images




Mirror
+n −4
+n −4
Co
Co