

Isomerism in coordination complexes

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graph TD; A[Isomerism in coordination complexes] --> B[Structural isomerism]; A --> C[Stereoisomerism]; B --> B1[Ionization isomerism]; B --> B2[Hydration isomerism]; B --> B3[Coordination isomerism]; B --> B4[Linkage isomerism]; C --> C1[Diastereoisomers]; C --> C2[Enantiomers];
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Structural isomerism

Ionization isomerism
Hydration isomerism
Coordination isomerism
Linkage isomerism

Stereoisomerism

Diastereoisomers
Enantiomers

Gli isomeri strutturali differiscono fra loro nelle connessioni fra gli atomi nelle molecole.

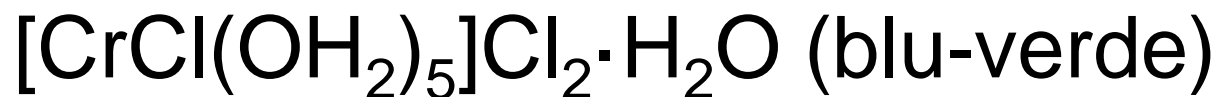
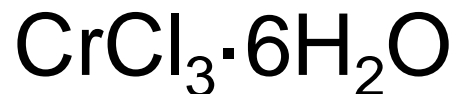
Gli stereoisomeri hanno le stesse connessioni, ma differiscono per l'arrangiamento degli atomi nello spazio.

Isomeri di ionizzazione

$[\text{CoCl}_2(\text{en})_2]\text{NO}_2$ (verde)
 $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{SO}_4)$ (violetto)

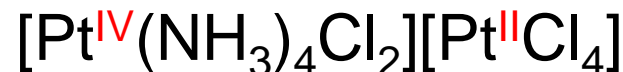
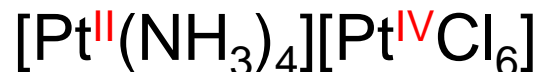
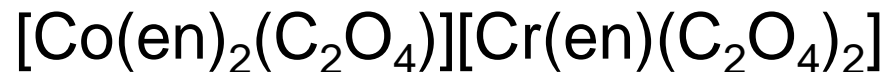
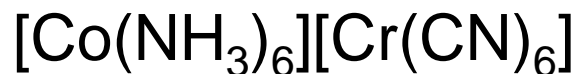
$[\text{CoCl}(\text{NO}_2)(\text{en})_2]\text{Cl}$ (rosso)
 $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$ (rosso)

Isomeri di idratazione

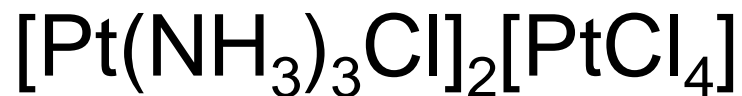
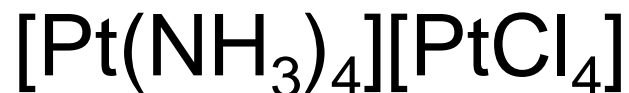
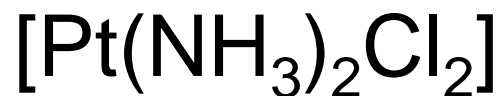


Isomeri di coordinazione

(quando sia anione che catione sono dei complessi)



Isomeri di polimerizzazione



Isomeri di legame (leganti ambidentati)

$-\text{NO}_2$ (nitro)

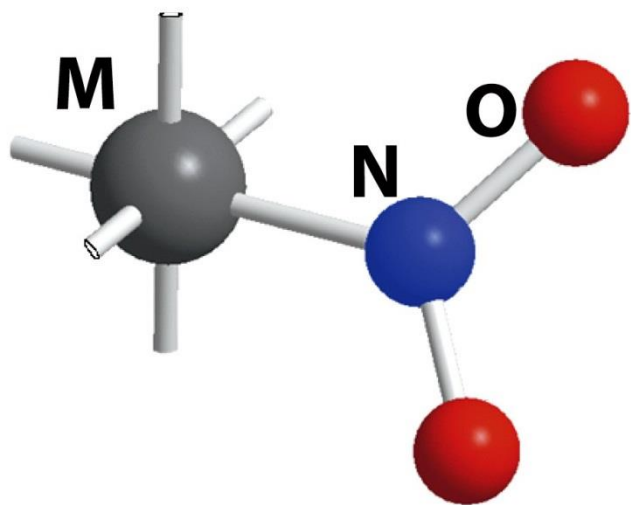
$-\text{C}\equiv\text{N}$ (nitrile)

$-\text{S}-\text{C}\equiv\text{N}^-$ (tiocianato)

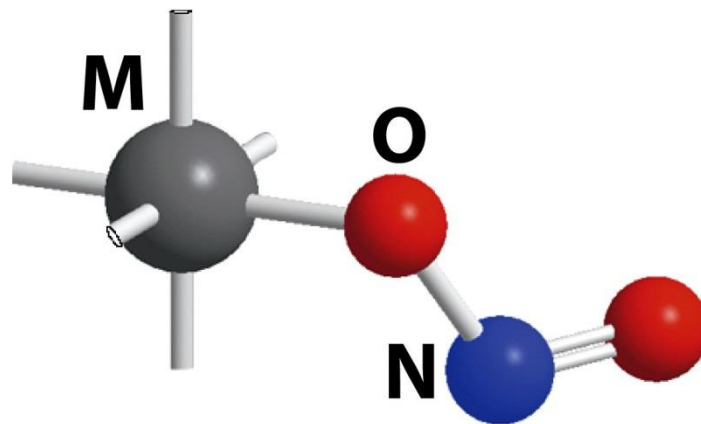
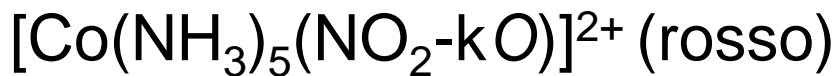
$-\text{O}-\text{NO}$ (nitrito)

$-\text{N}\equiv\text{C}$ (isonitrile)

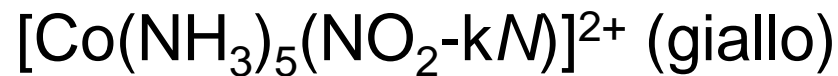
$-\text{N}=\text{C}=\text{S}^-$ (isotiocianato)

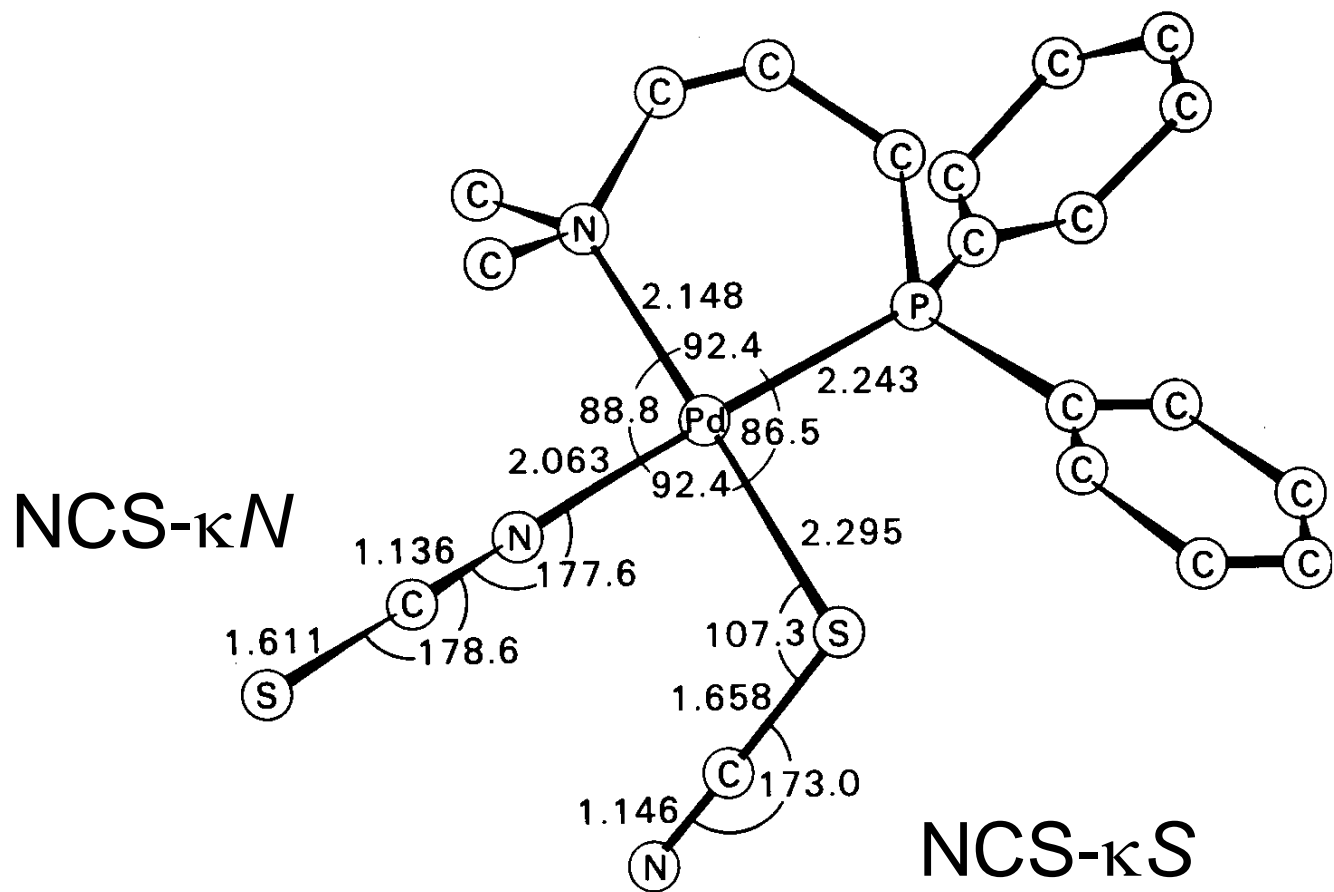


Nitro ligand

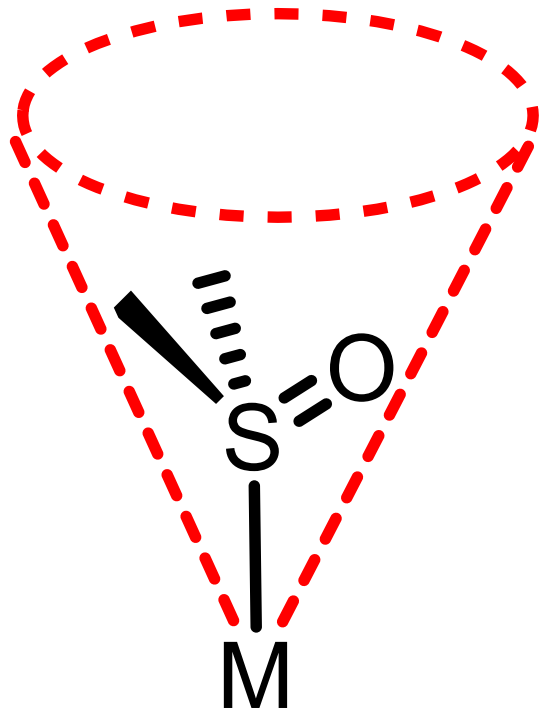


Nitrito ligand

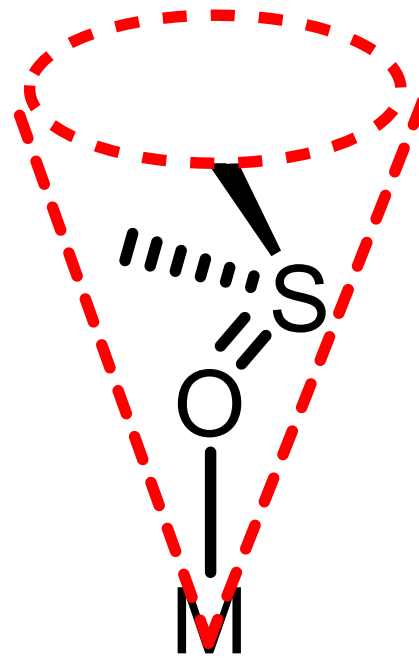




Angolo di cono dei leganti



$$\theta = 112^\circ$$



$$\theta = 100^\circ$$

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Structural isomerism

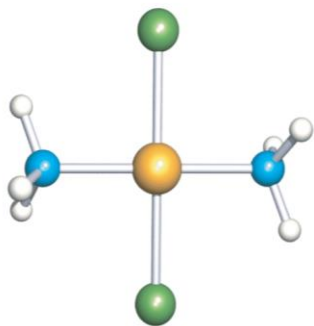
Stereoisomerism

Ionization isomerism
Hydration isomerism
Coordination isomerism
Linkage isomerism

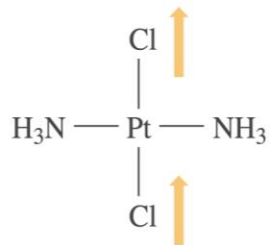
Diastereoisomers
Enantiomers

stereoisomeri che non siano enantiomeri sono diastereoisomeri

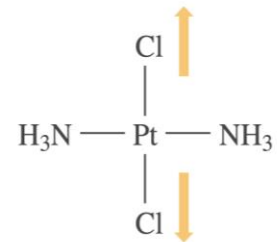
i diastereoisomeri hanno fra loro proprietà fisiche e chimiche diverse



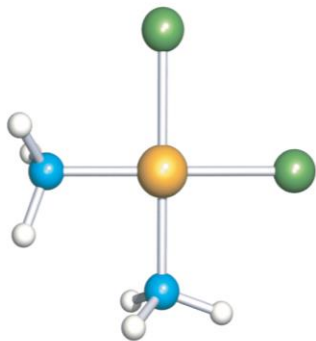
The *trans*-isomer is non-polar



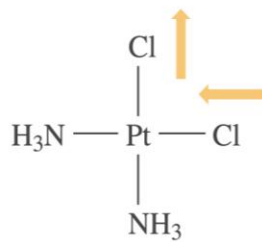
Asymmetric stretch:
IR active
 365 cm^{-1}



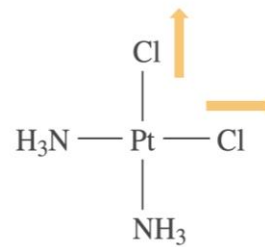
Symmetric stretch:
IR inactive



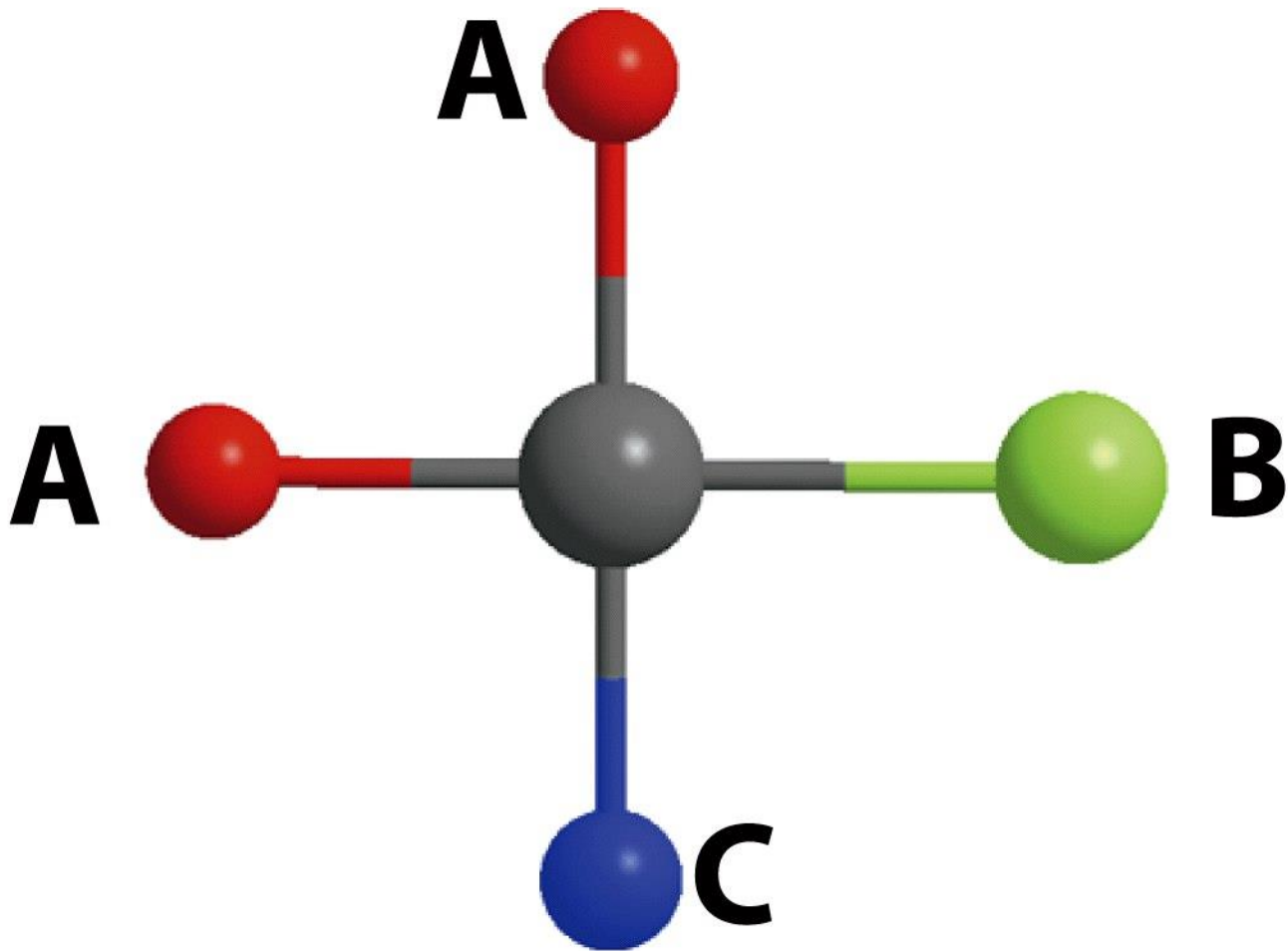
The *cis*-isomer is polar



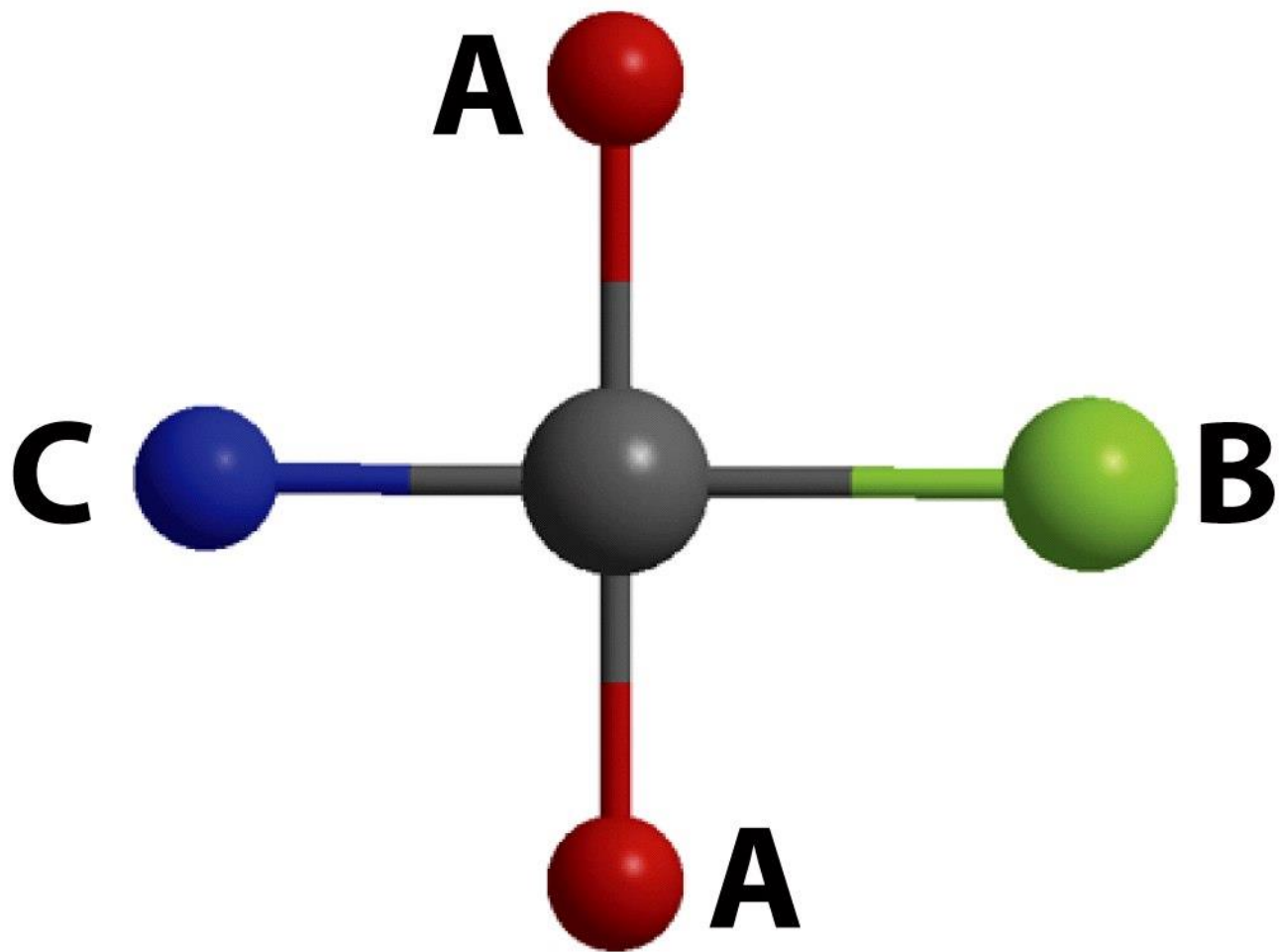
Asymmetric stretch:
IR active
 330 cm^{-1}



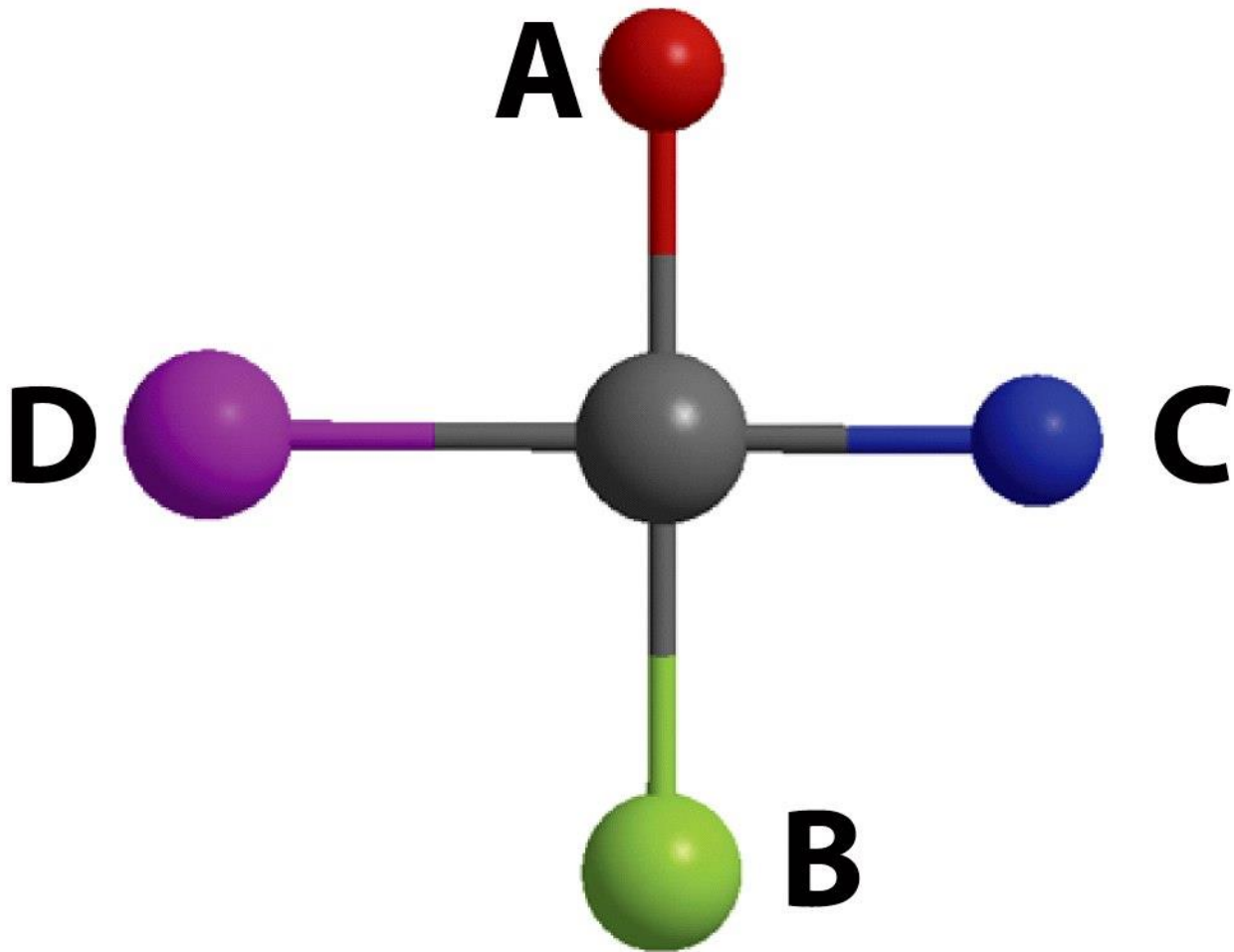
Symmetric stretch:
IR active
 323 cm^{-1}



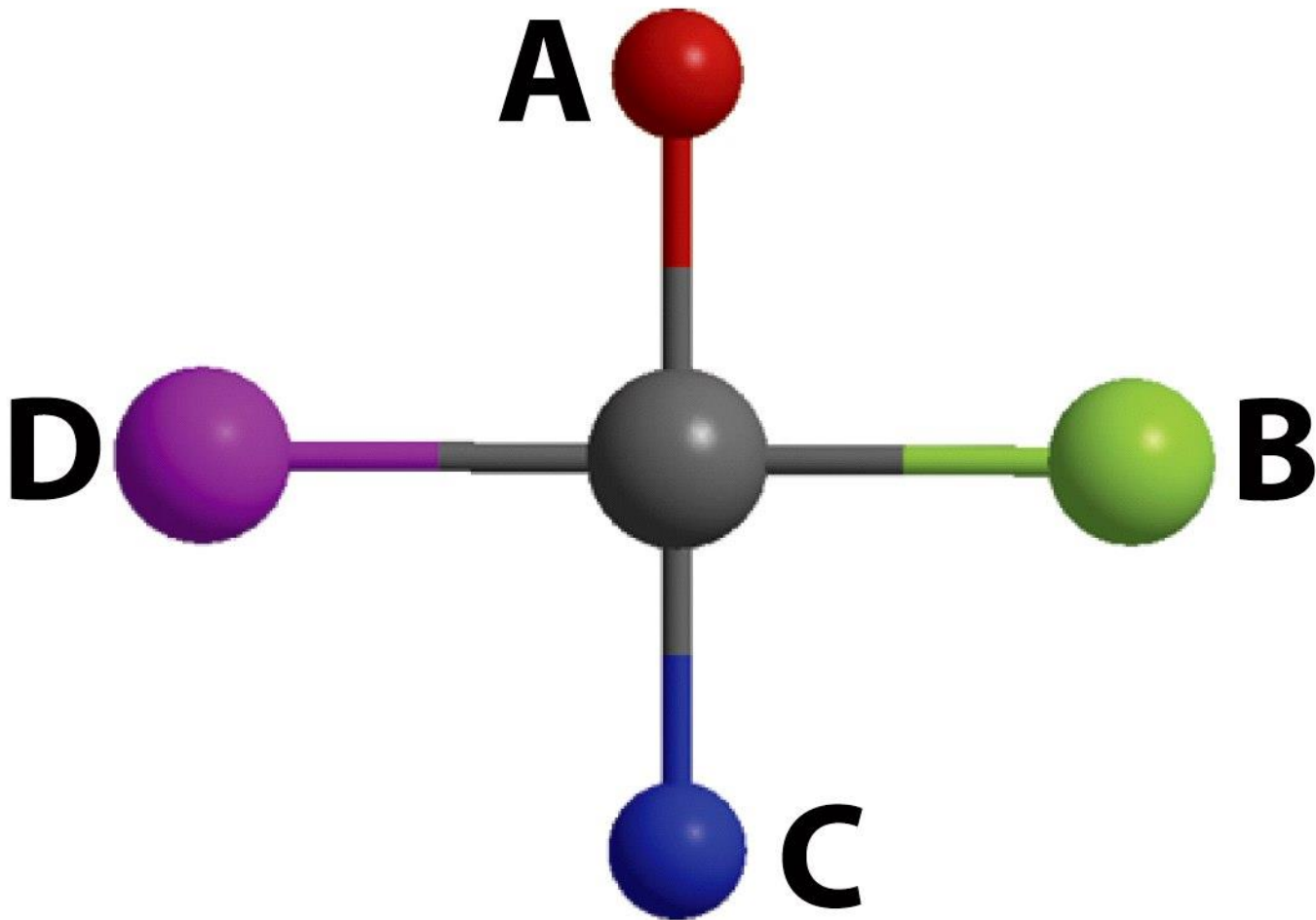
***cis*-[MA₂BC]**



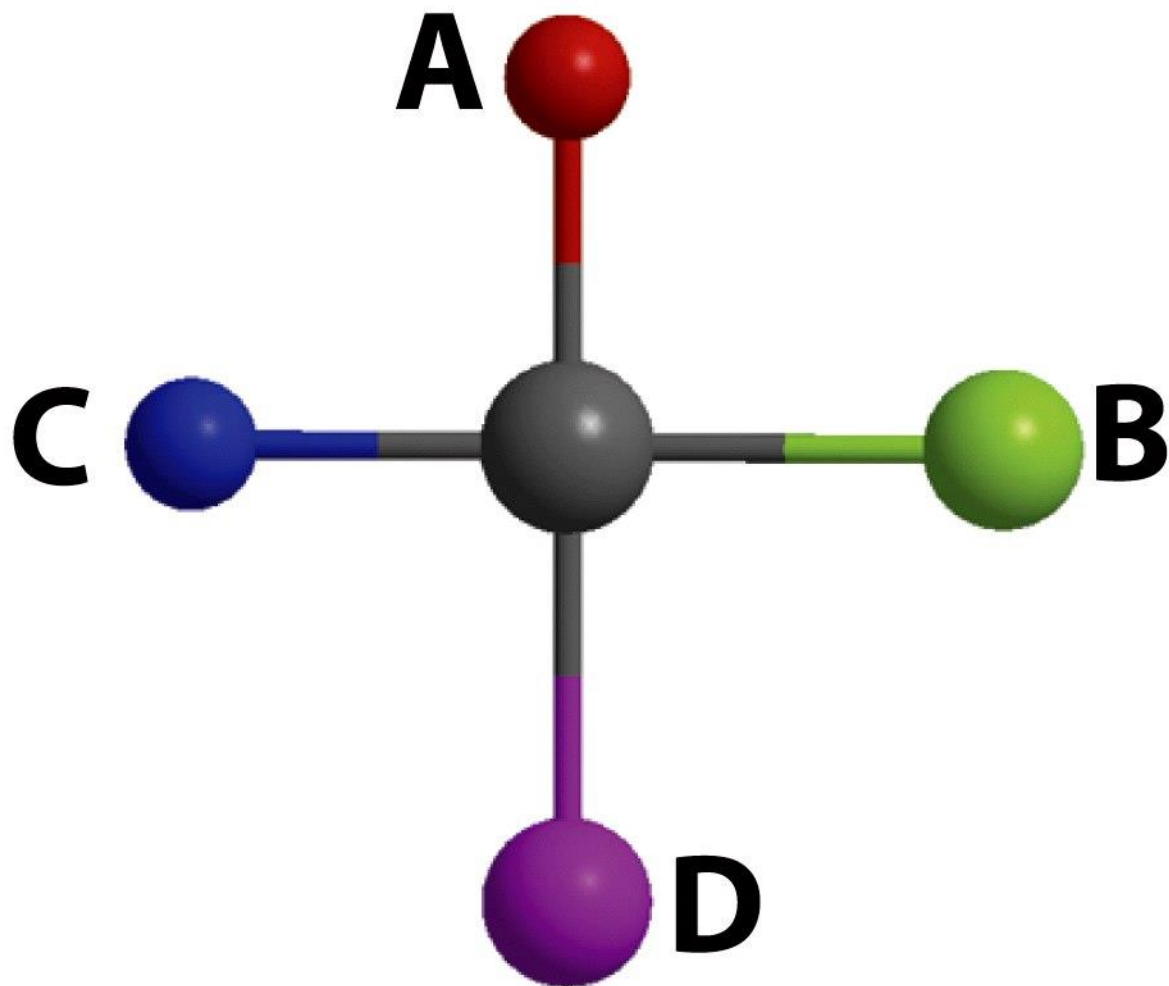
***trans*-[MA₂BC]**



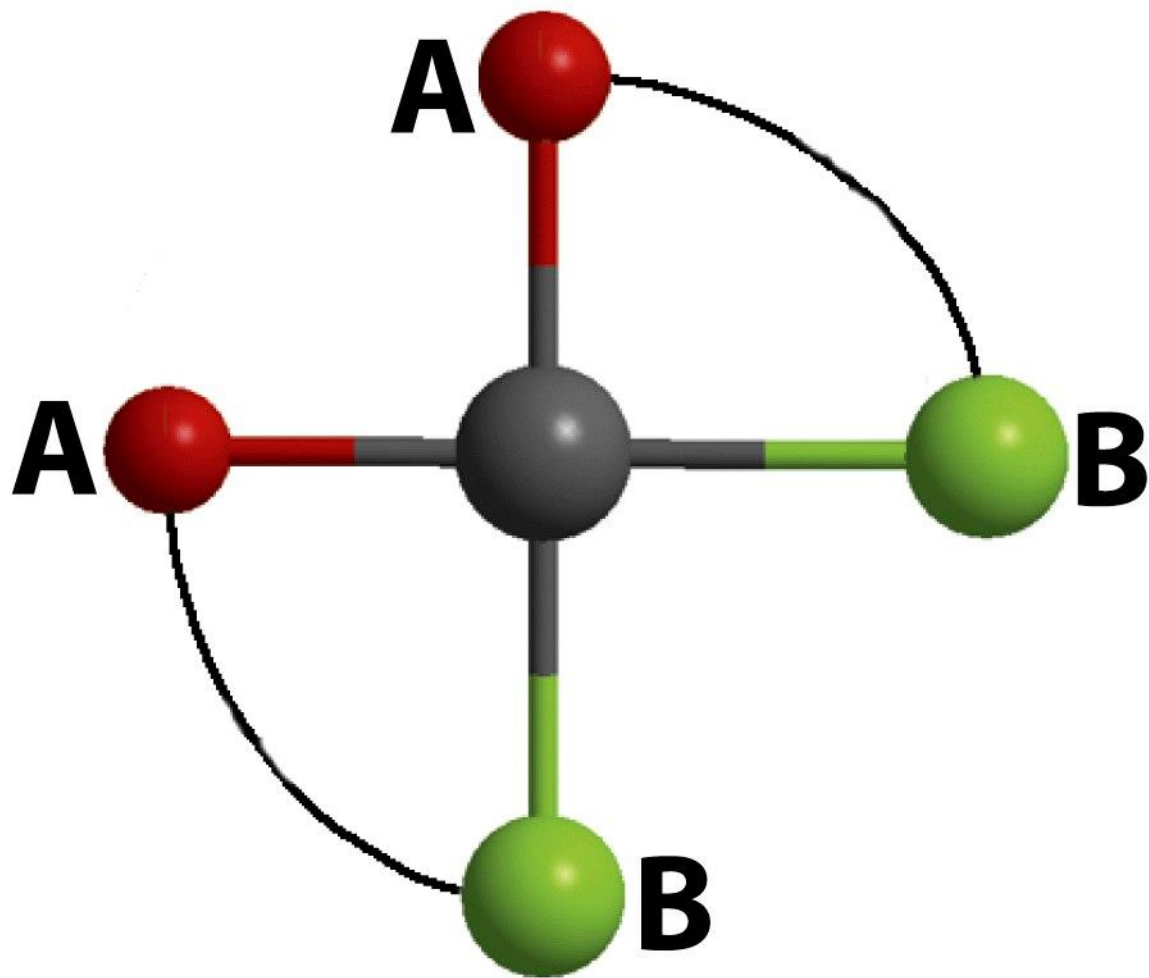
[MABCD], A *trans* to B

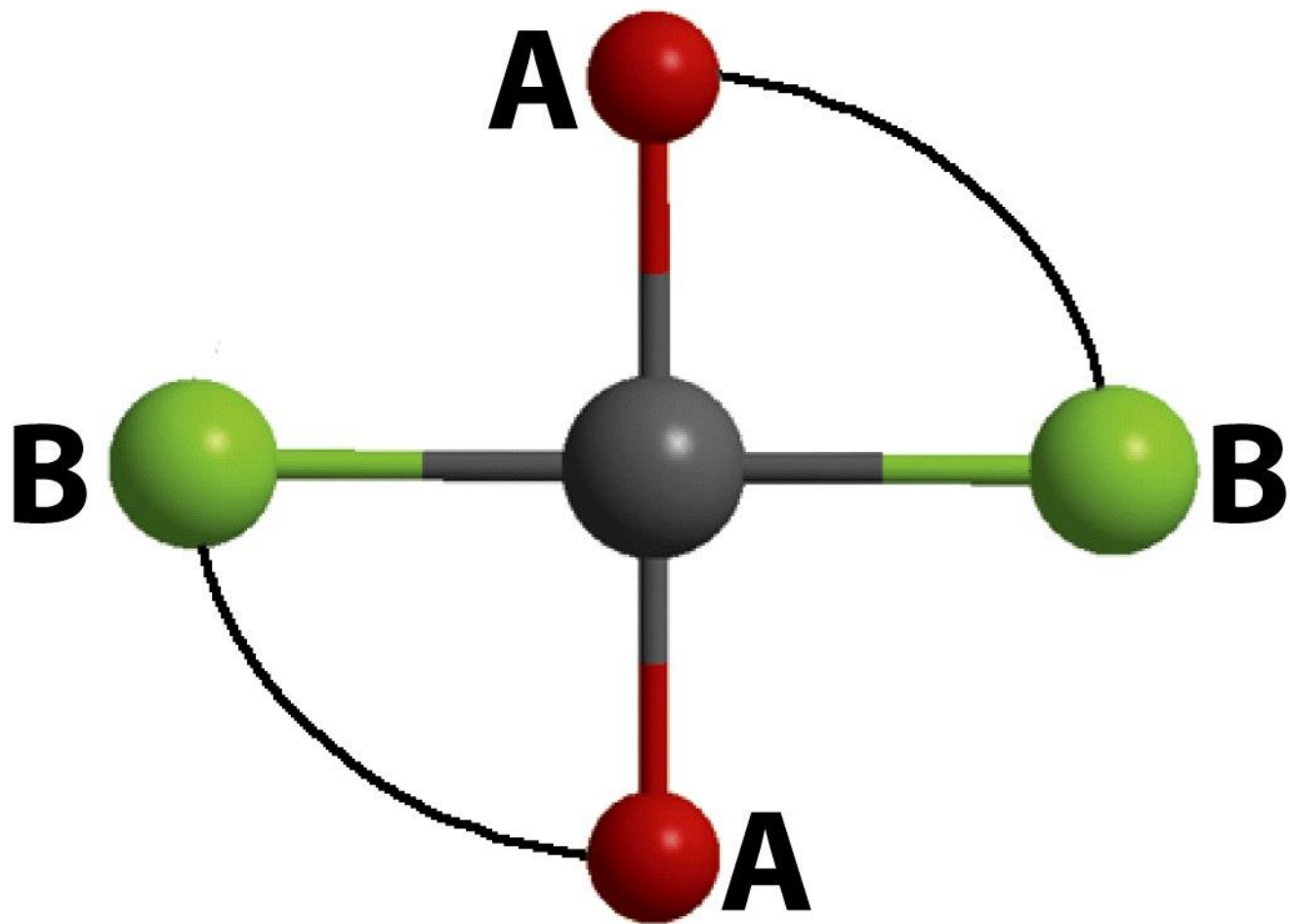


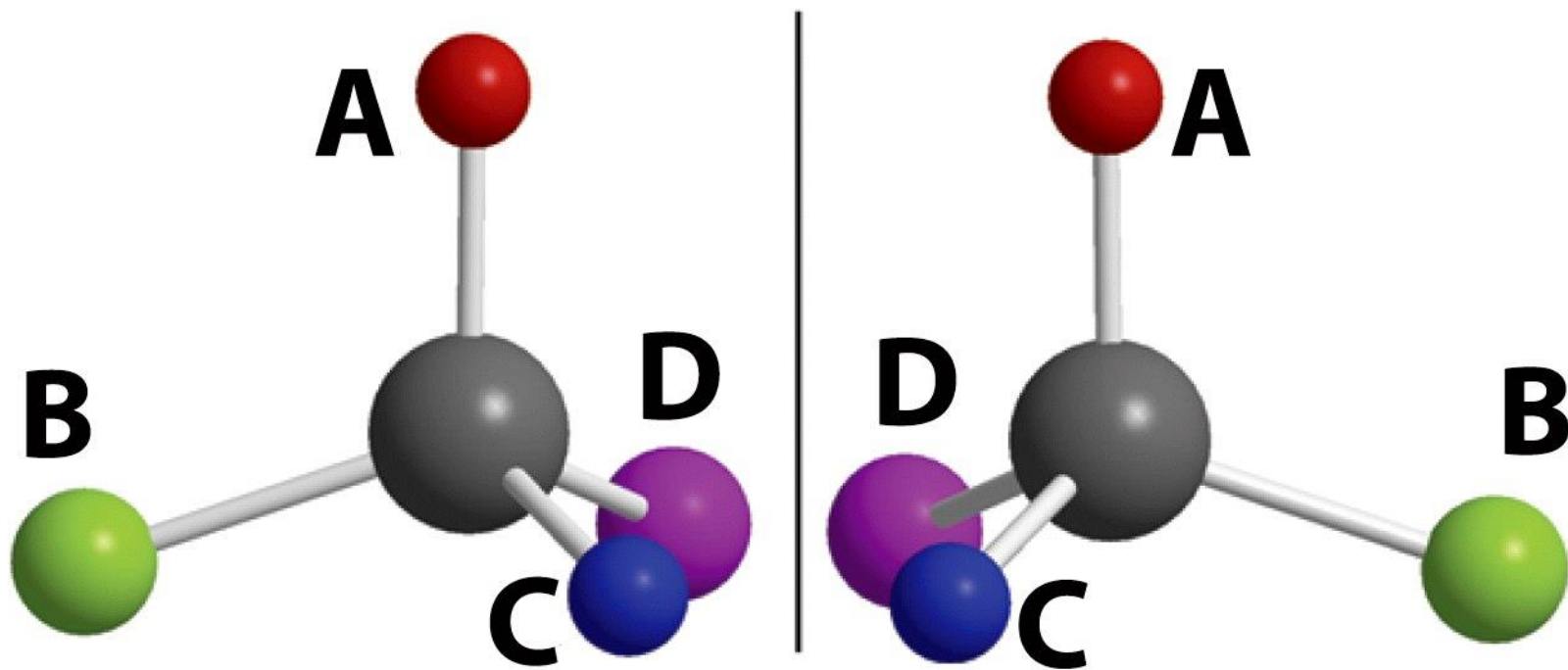
[MABCD], *A trans to C*



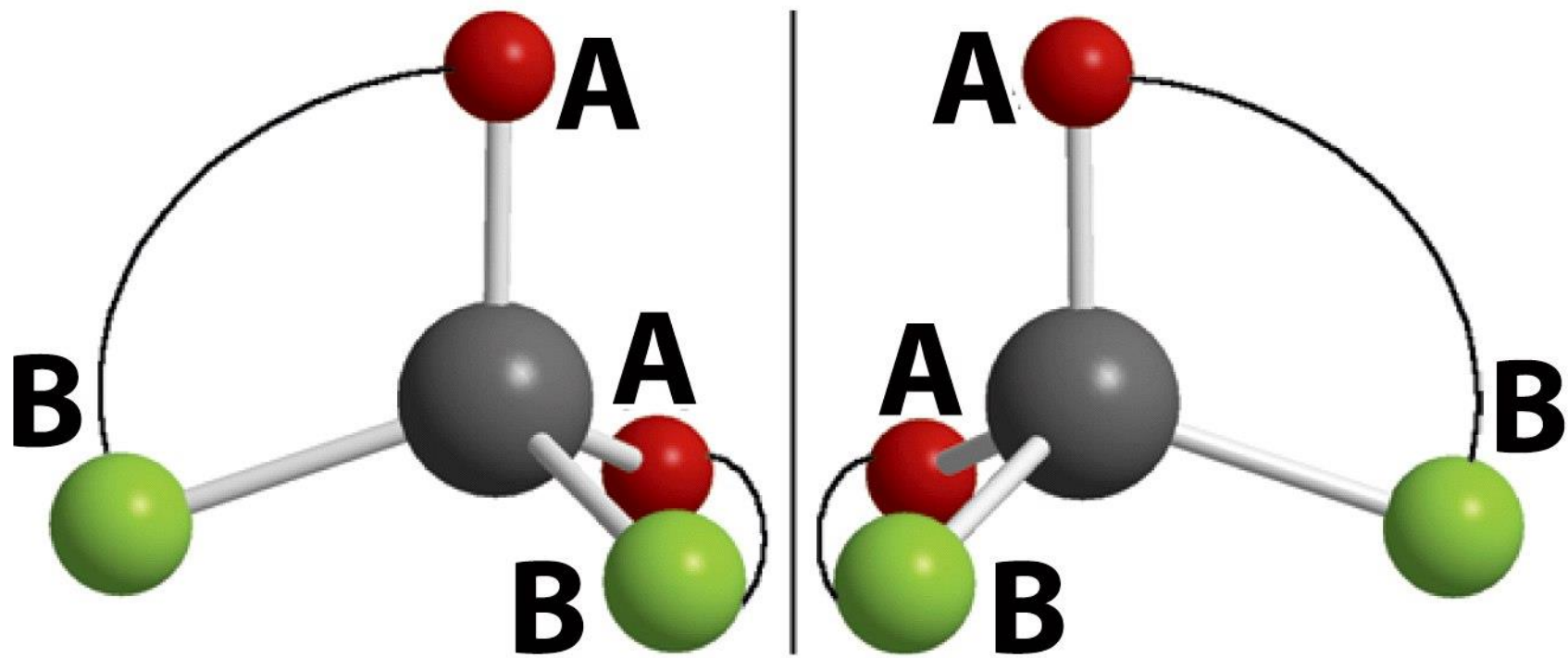
[MABCD], *A trans to D*



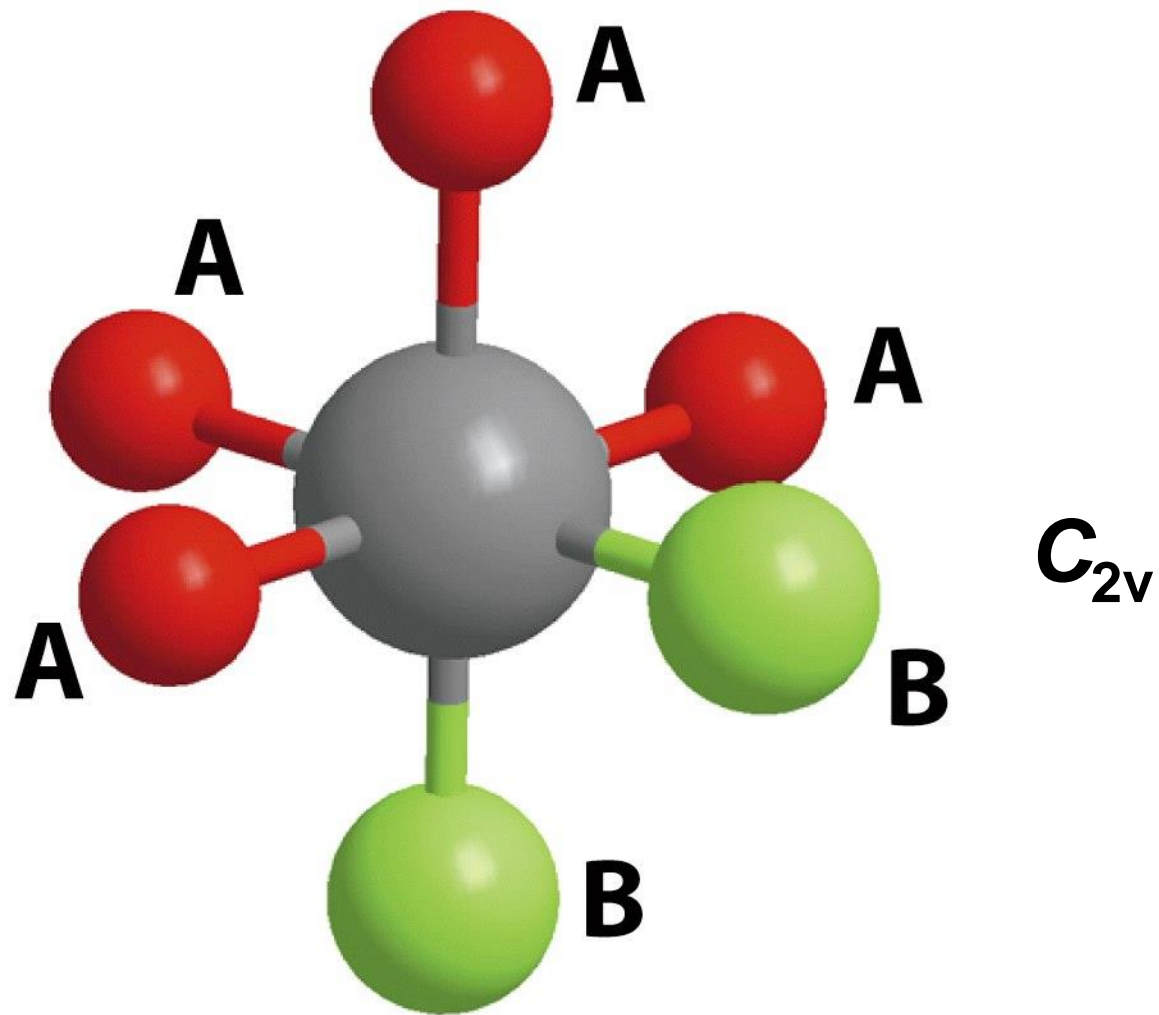


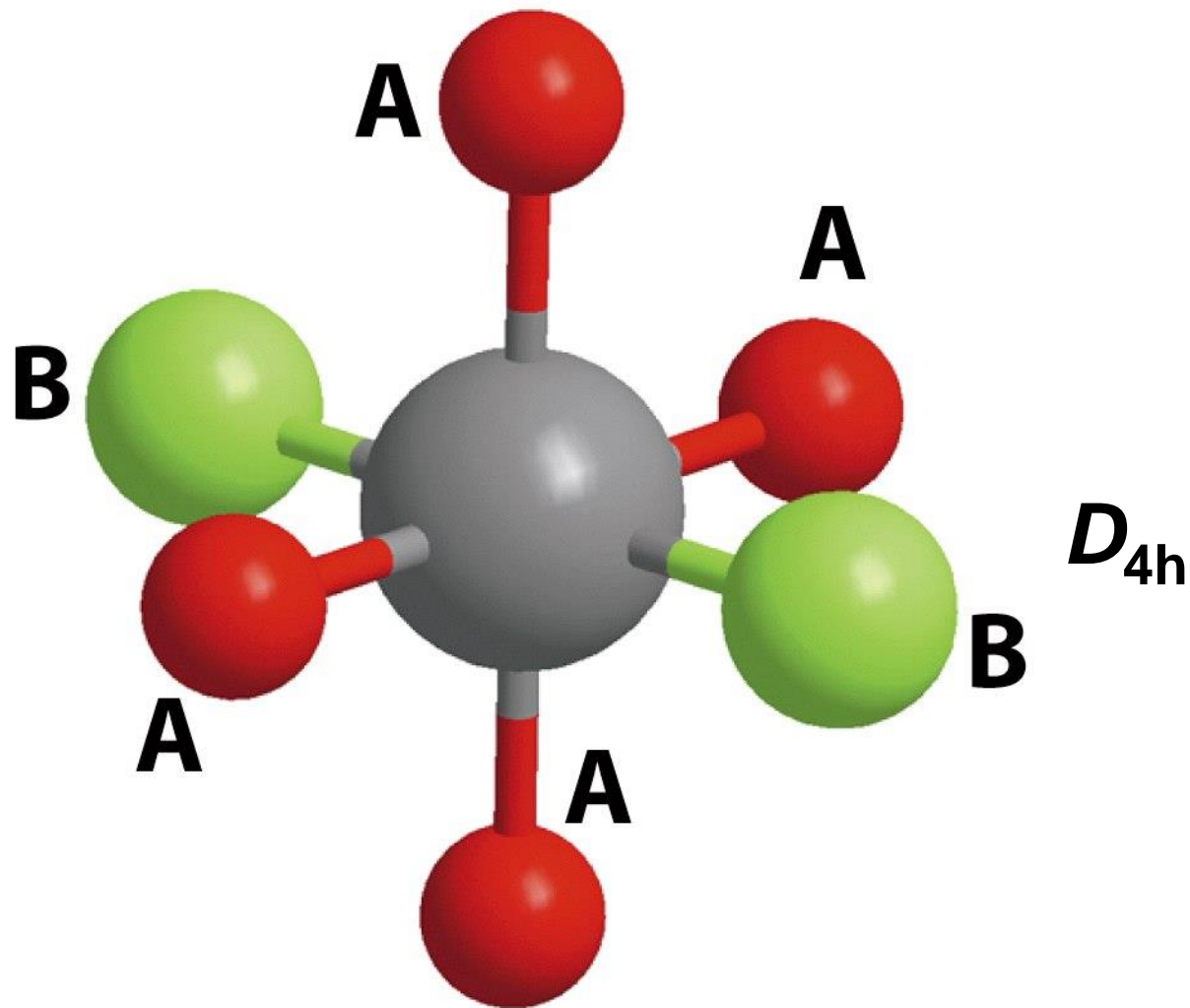


[MABCD] enantiomers

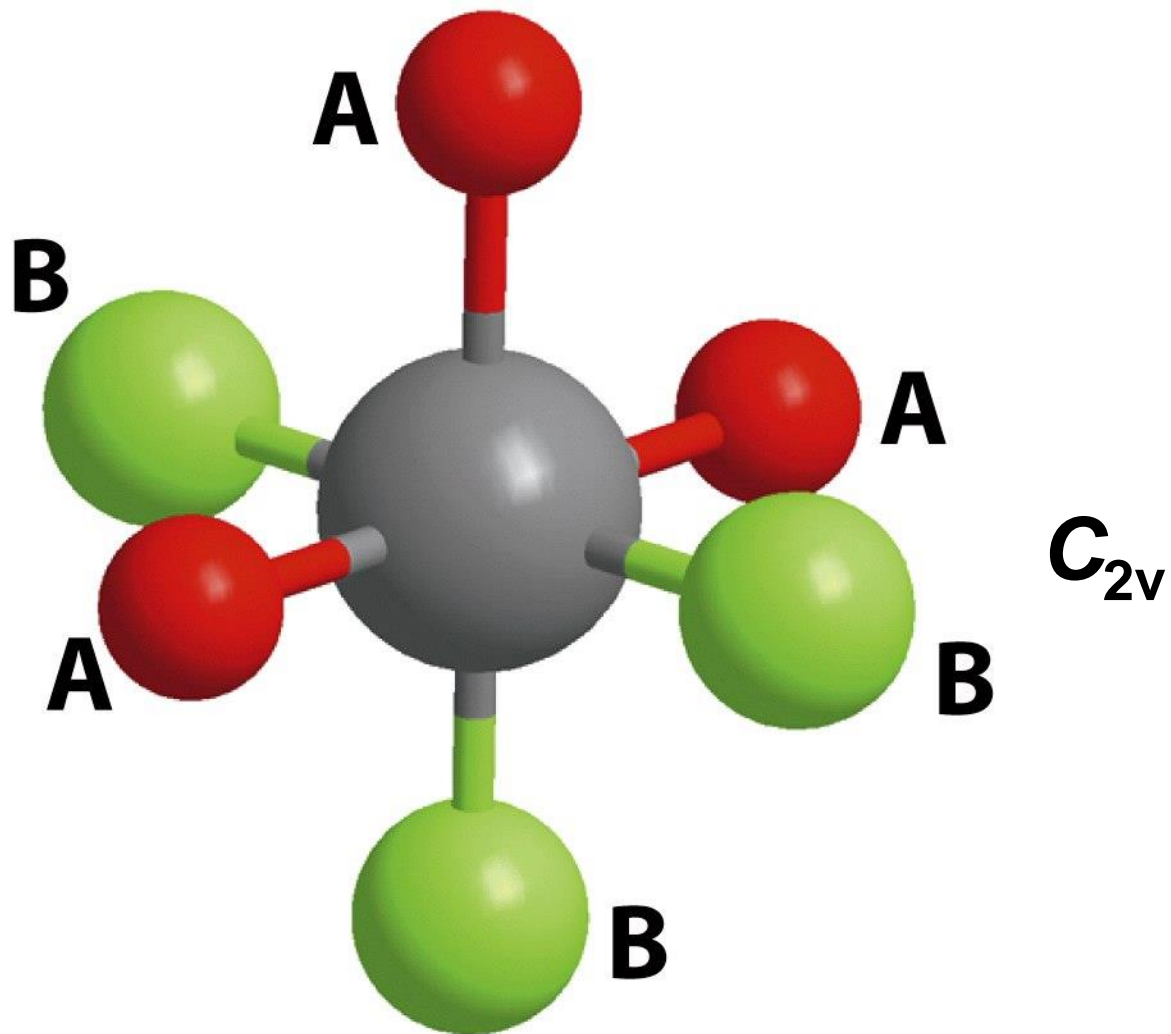


$[M(AB)_2]$ enantiomers

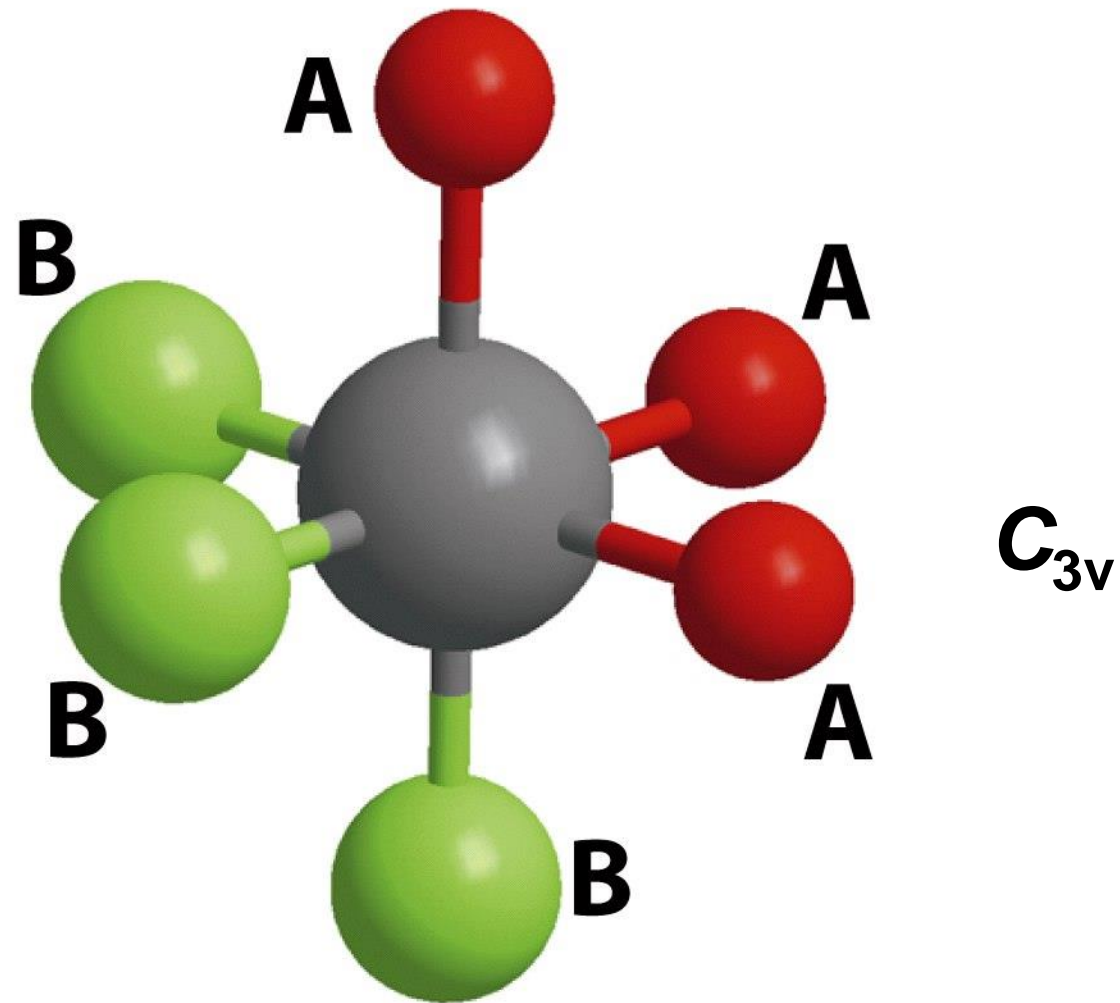




***trans*-[MA₄B₂]**

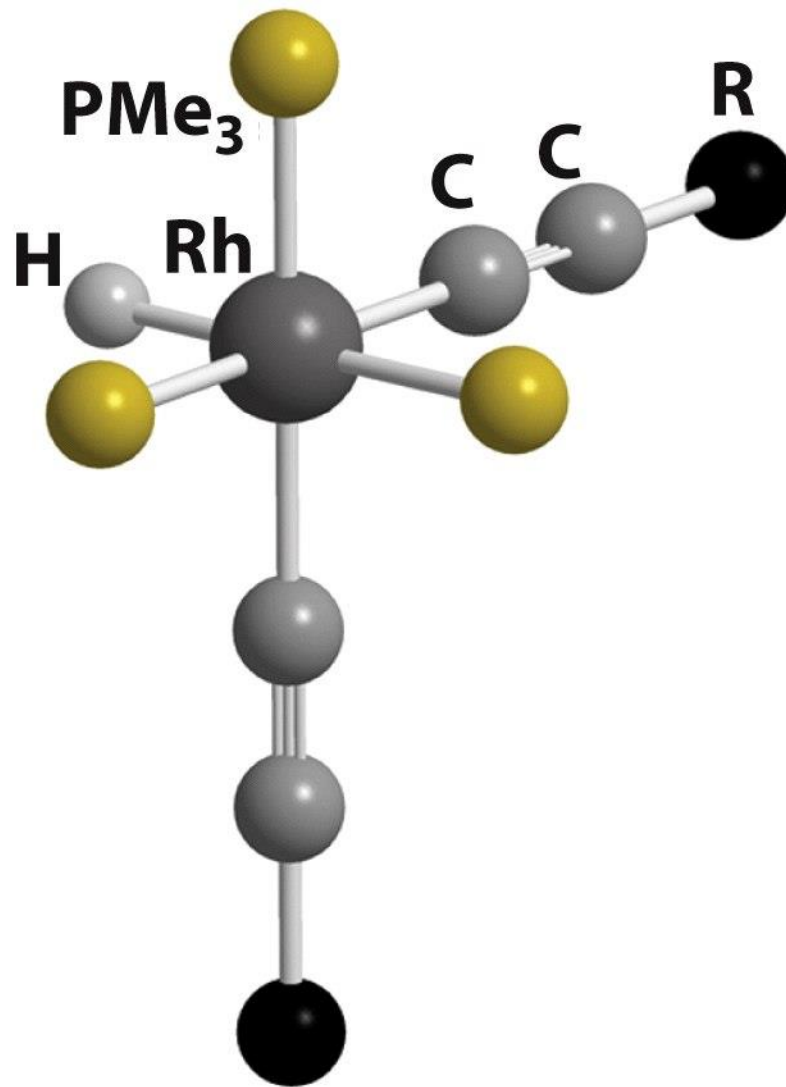


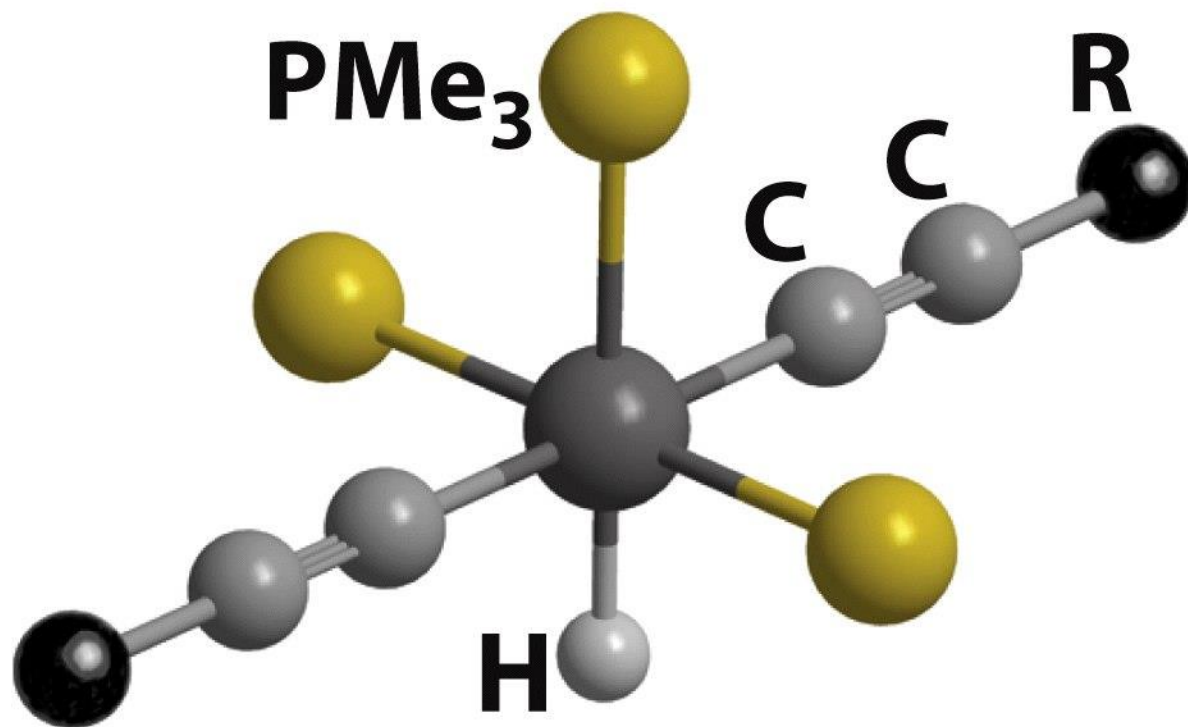
meridional

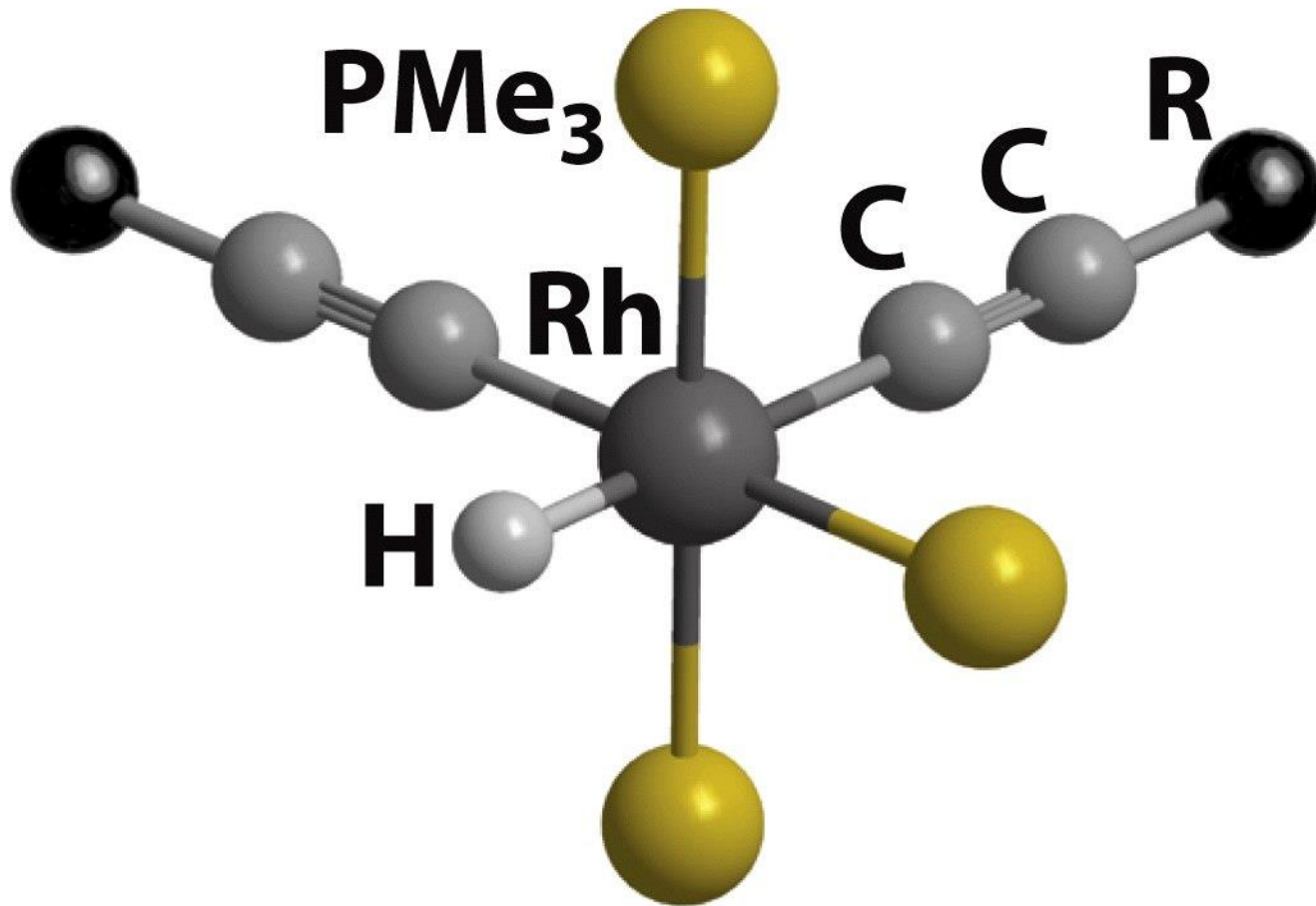


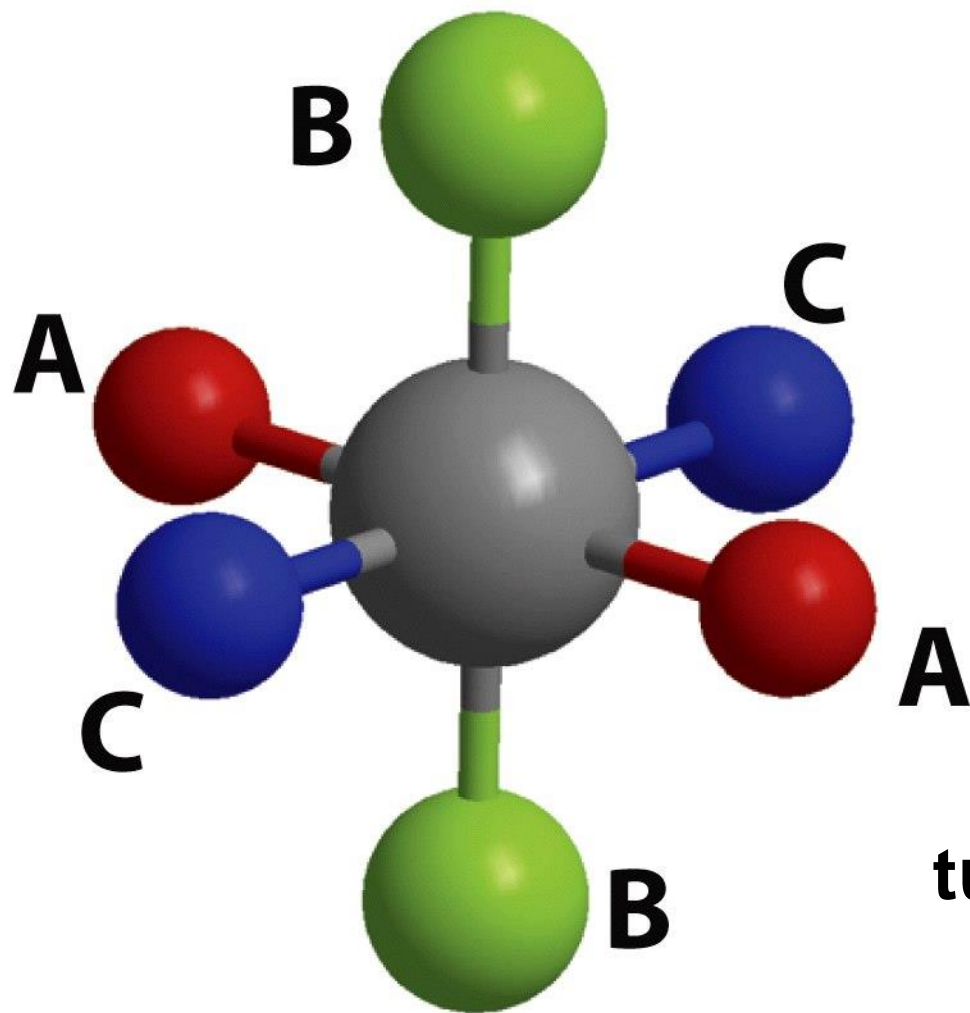
fac-[MA₃B₃]

facial



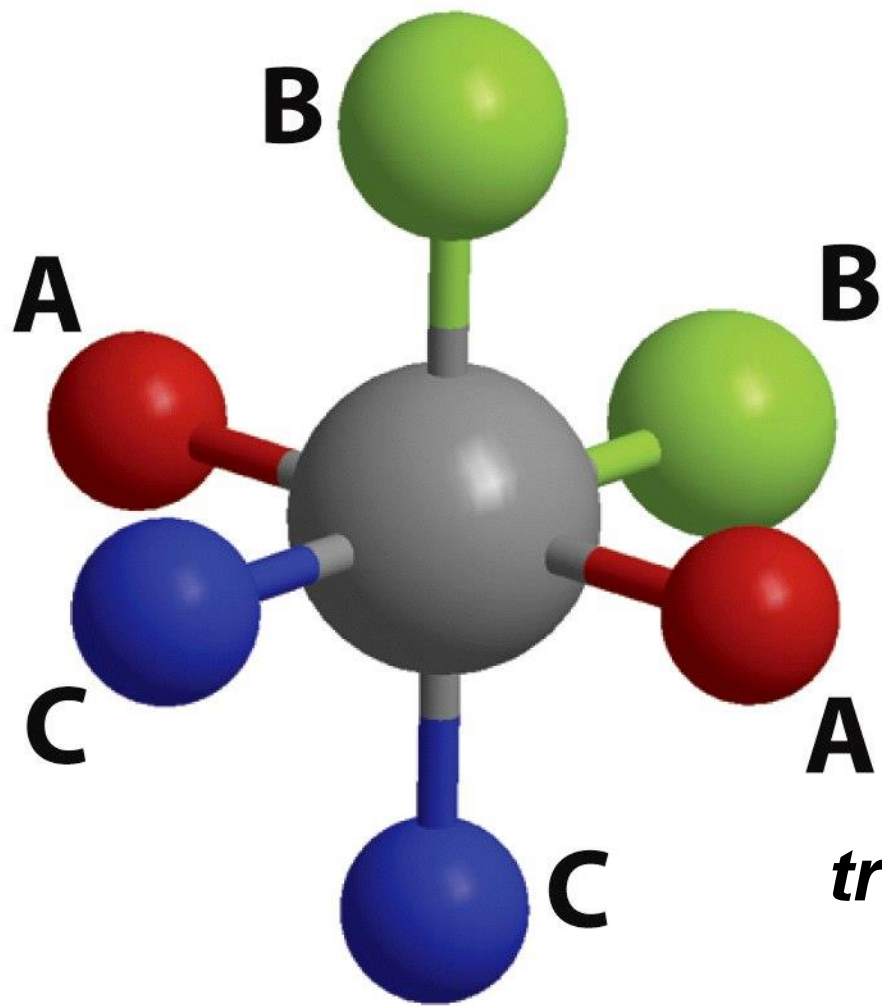






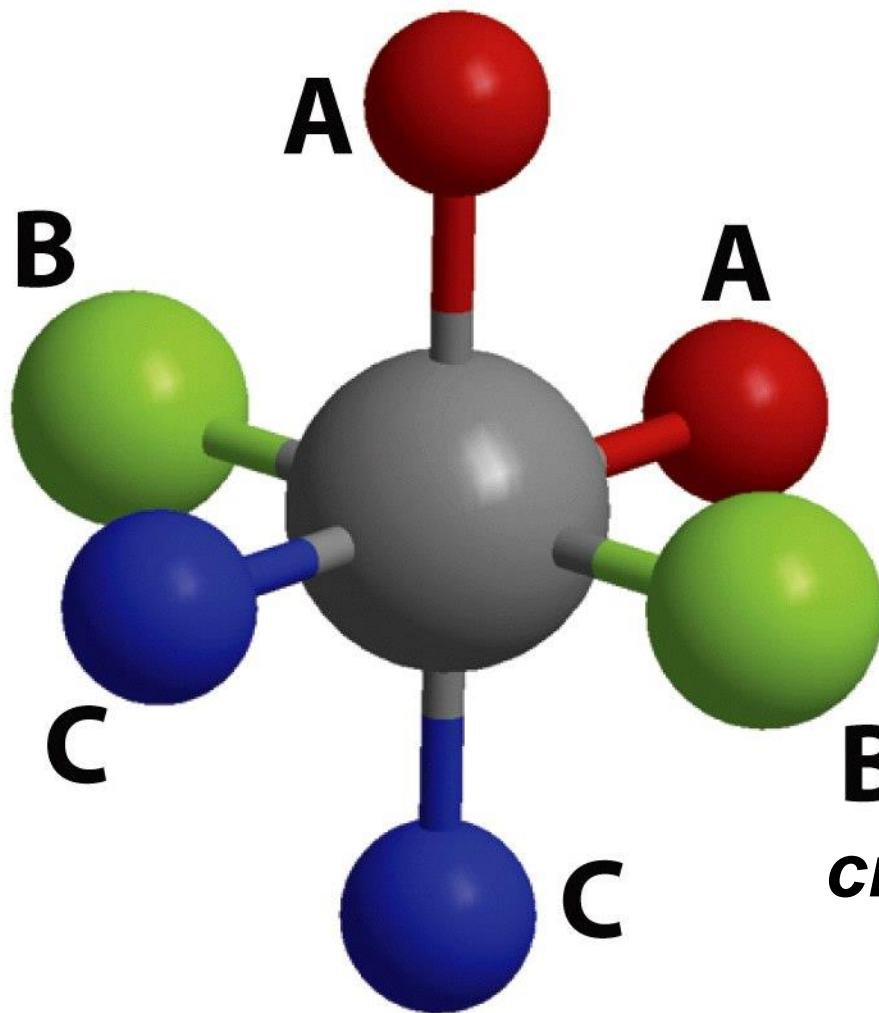
tutto-trans





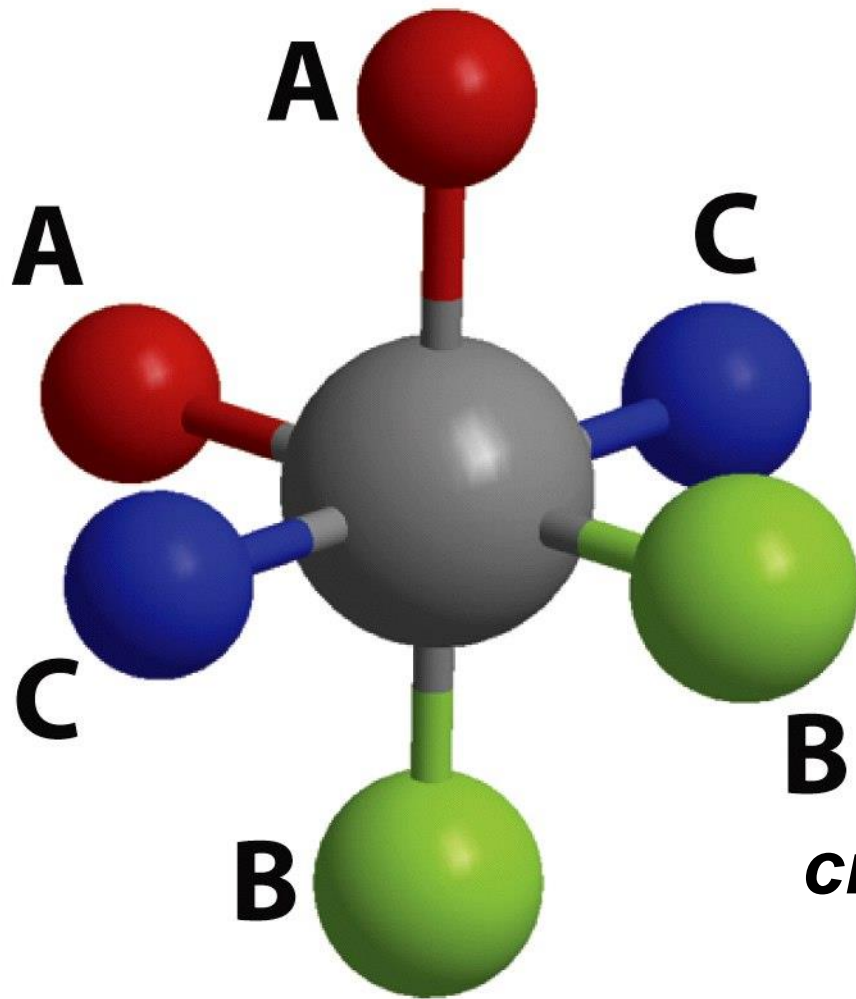
trans, cis, cis





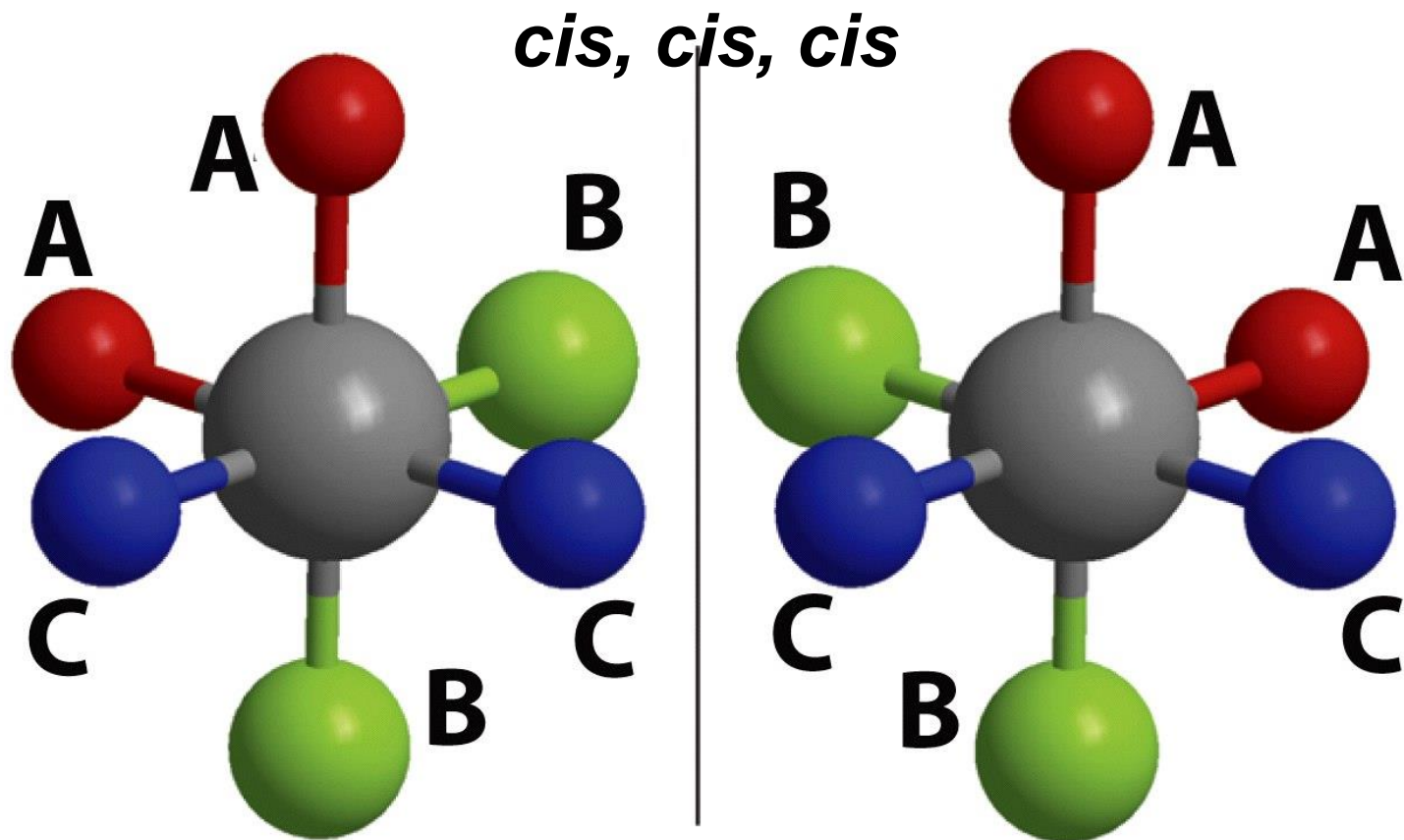
cis, trans, cis





cis, cis, trans





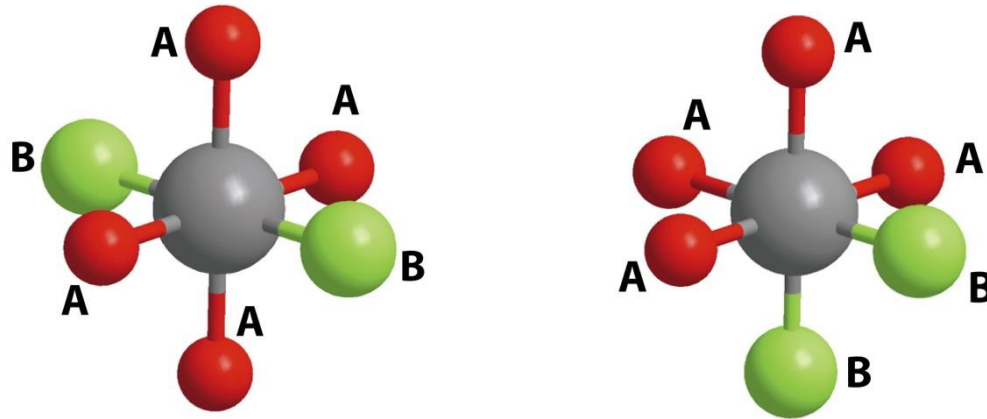
[MA₂B₂C₂] enantiomers

M = centro stereogenico

Descrittori A e C

*Un atomo di una molecola viene detto **stereogenico** se uno scambio di due leganti porta ad uno stereoisomero della molecola di partenza.*

Se lo stereoisomero che si ottiene è l'altro enantiomero di una coppia, allora l'atomo stereogenico è un centro chirale

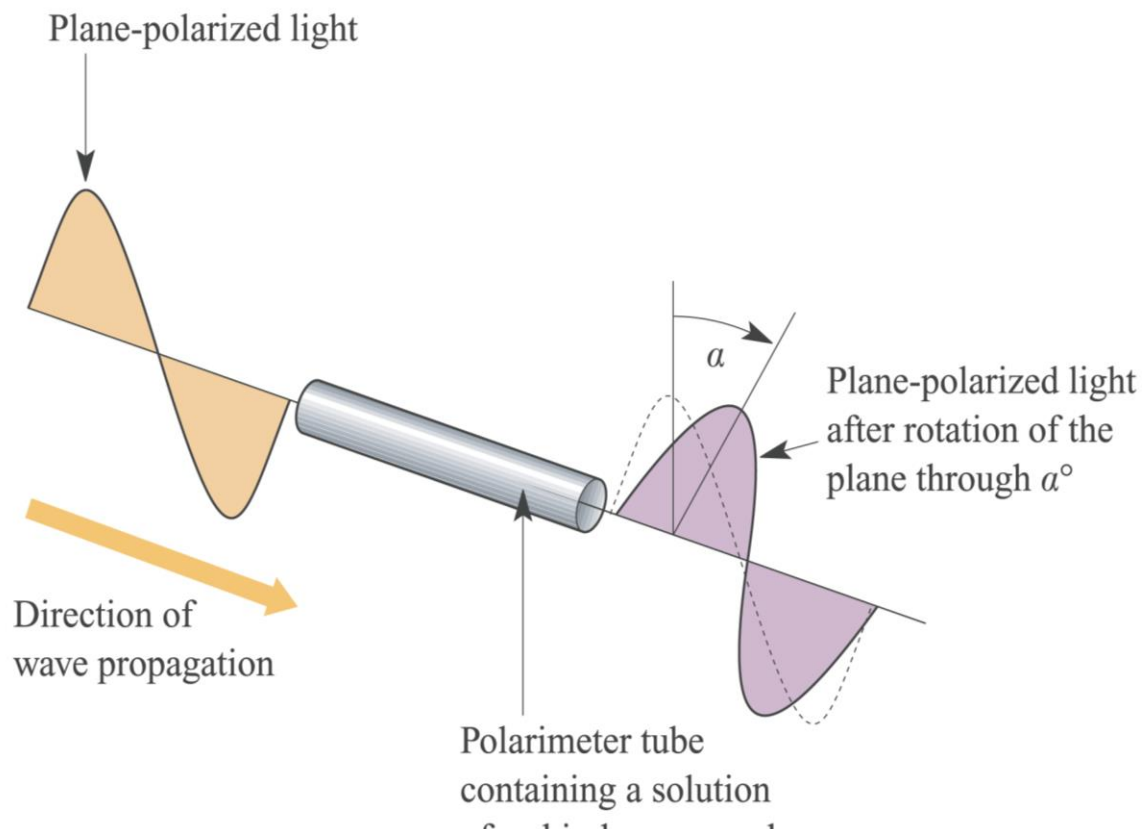


M = centro stereogenico non-chirale

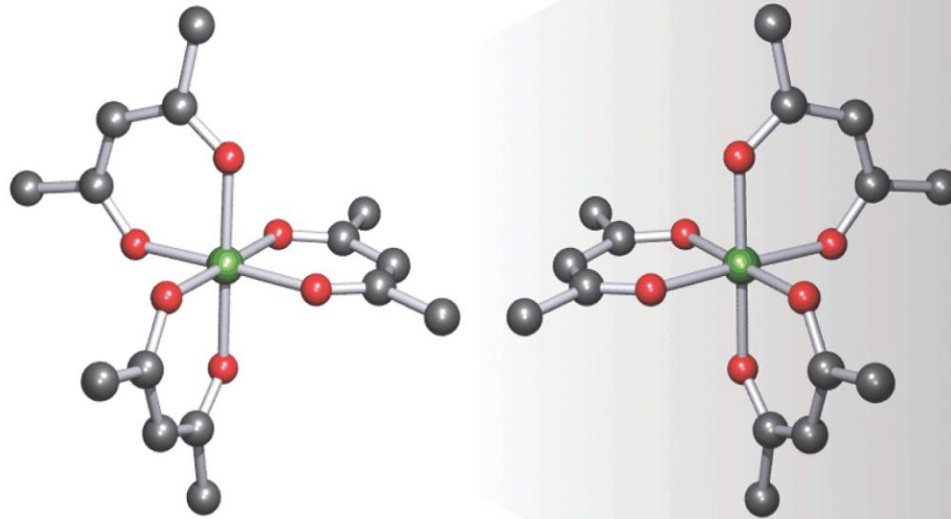
Enantiomeri

- *in un ambiente achirale gli enantiomeri si comportano allo stesso modo;*
- *in un ambiente chirale non racemico (e.g. ambiente biologico) gli enantiomeri si comportano in modo diverso*

- in un ambiente chirale ma racemico gli enantiomeri danno segno opposto per certe grandezze osservabili*



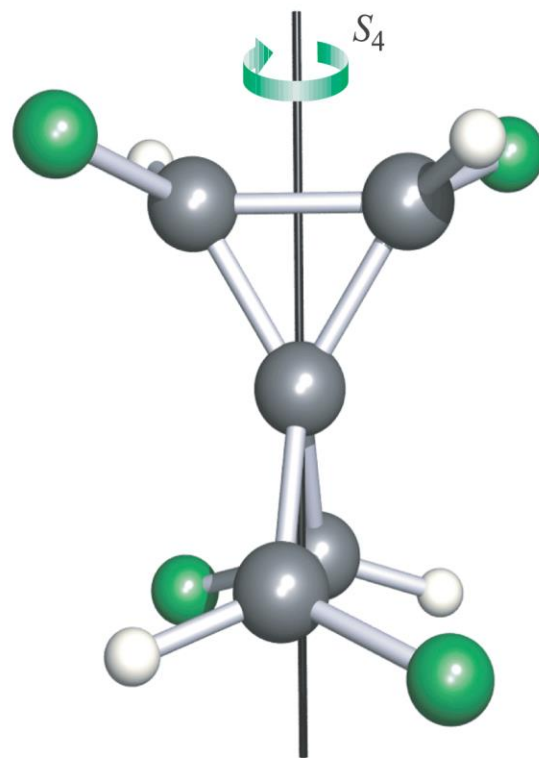
la luce polarizzata linearmente è un racemato di luce polarizzata circolarmente a destra e a sinistra



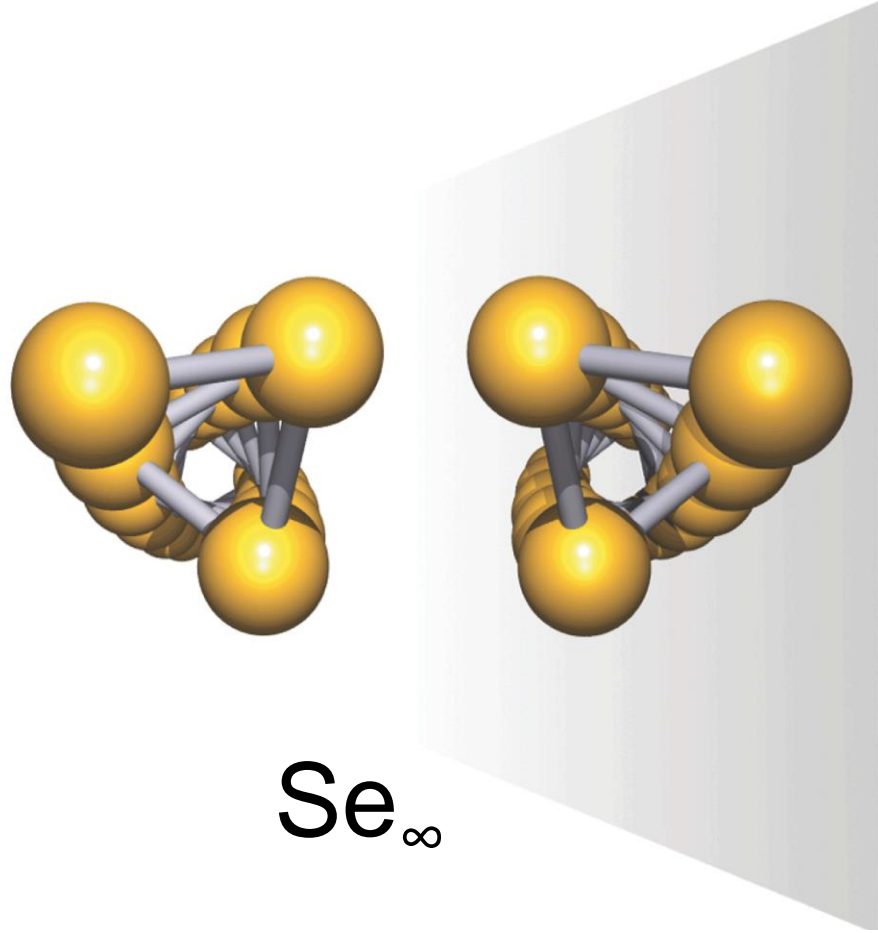
Δ -enantiomer

Λ -enantiomer

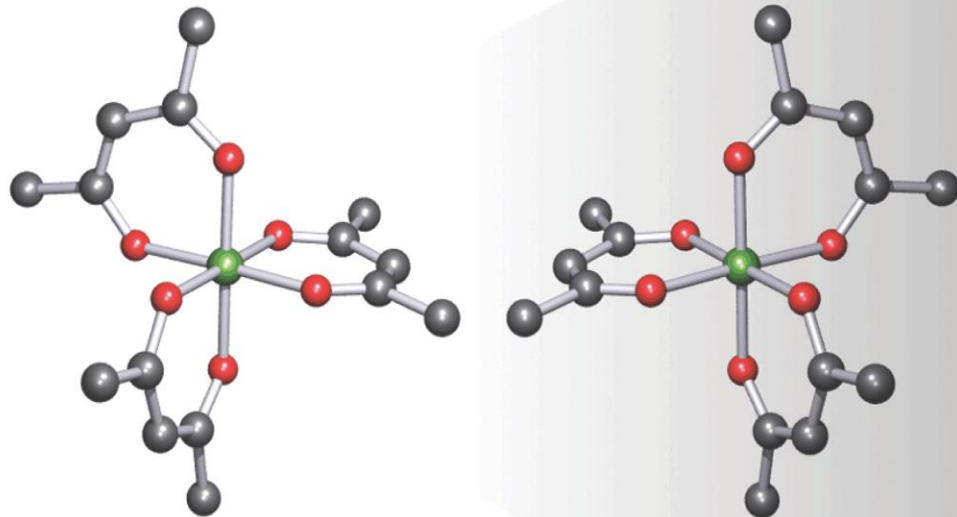
ogni molecola che non abbia S_n è chirale



Tetrafluoro-spiropentano, S_4 , achirale



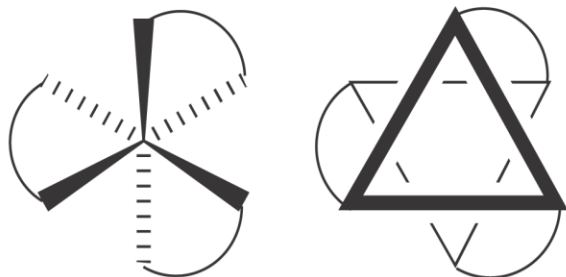
Se_8



Δ -enantiomer

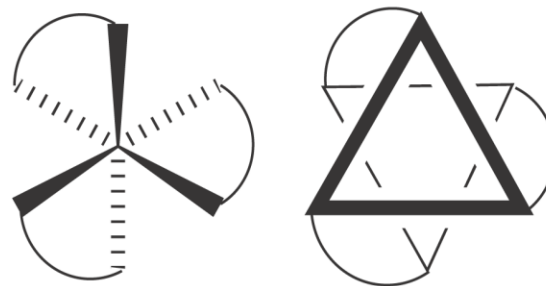
Λ -enantiomer

elica destrorsa

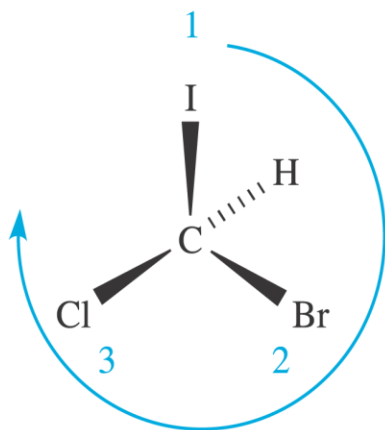


Δ

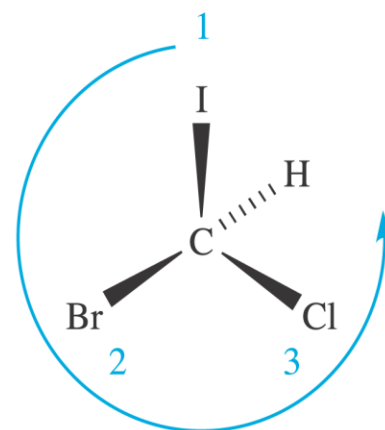
elica sinistrorsa



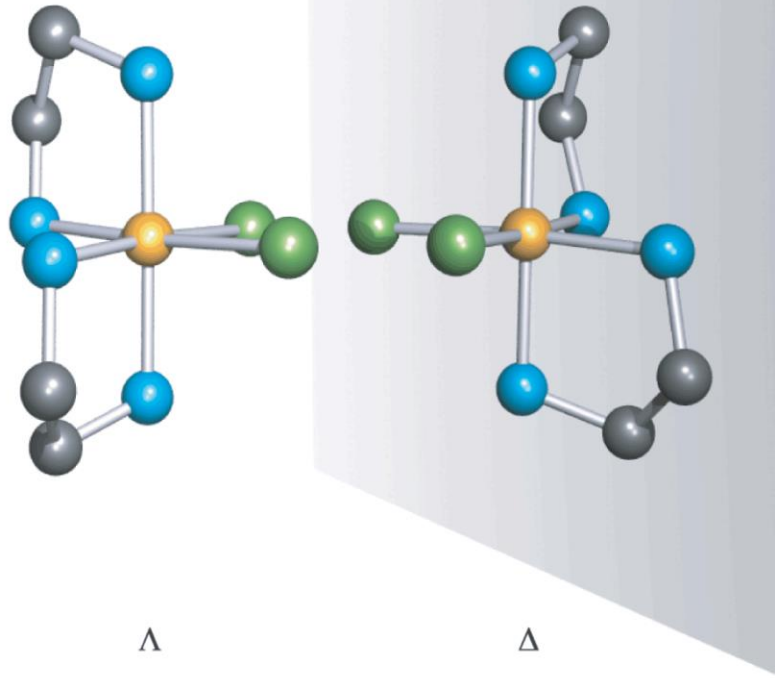
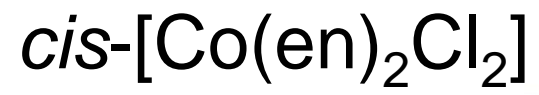
Λ

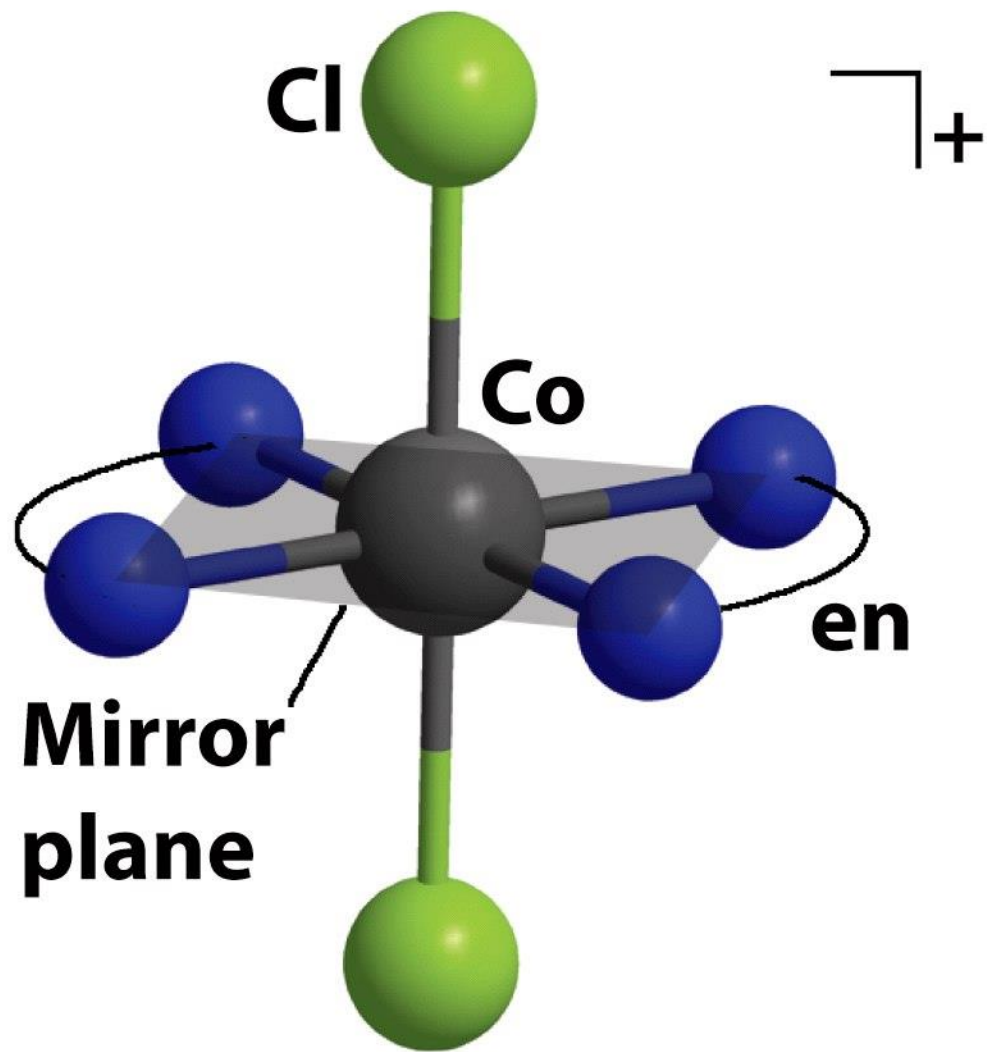


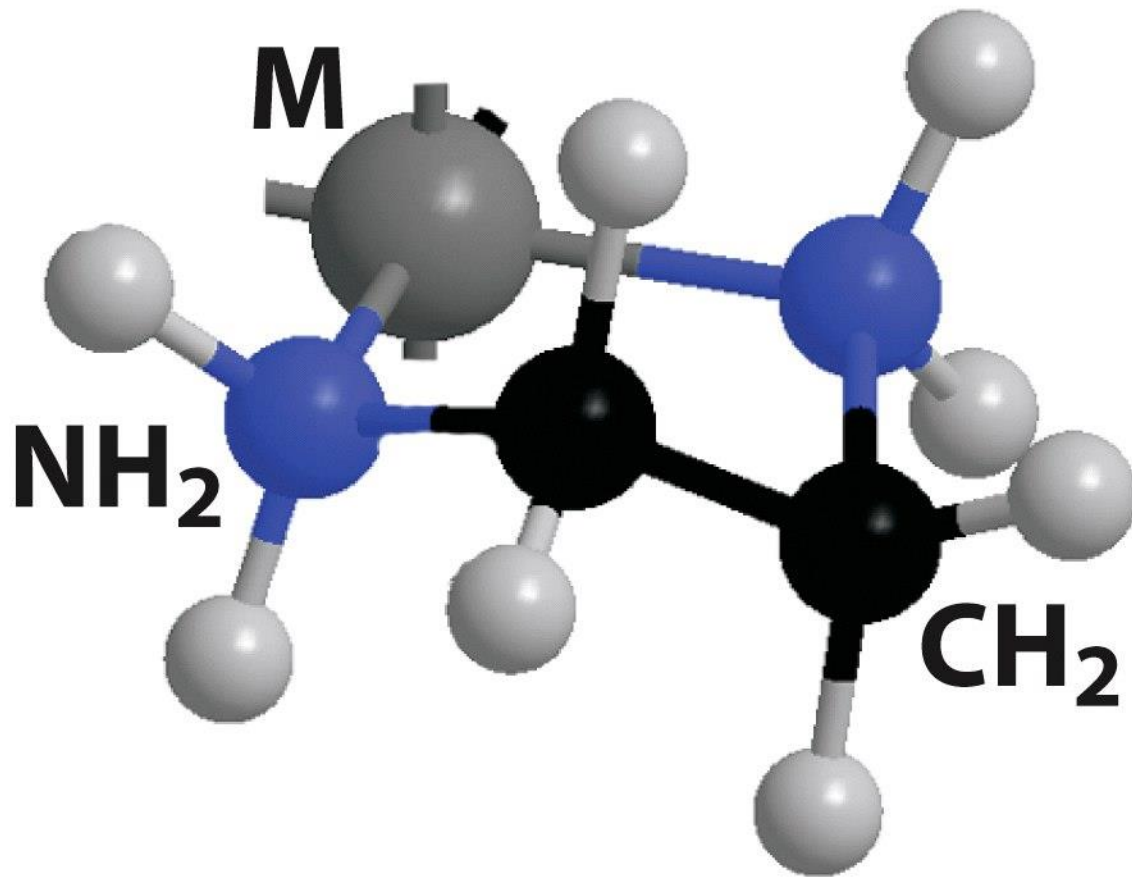
R



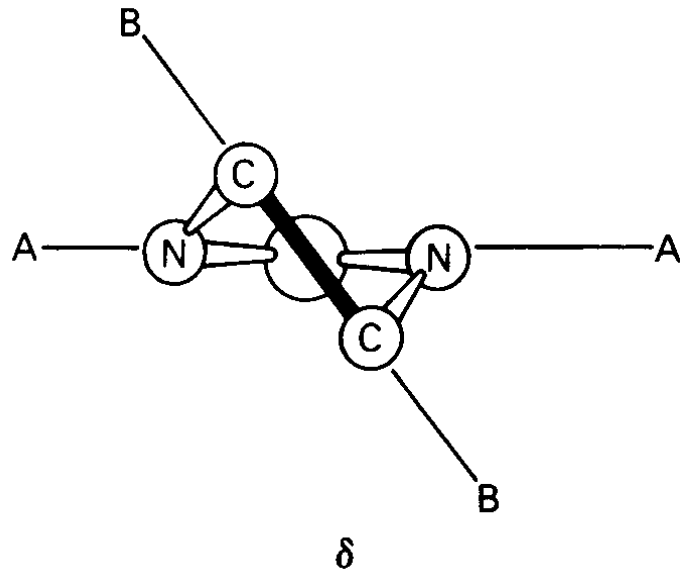
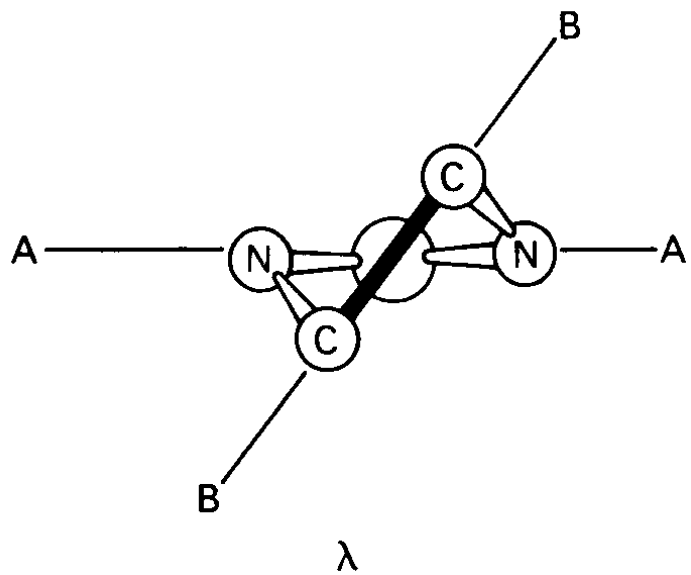
S

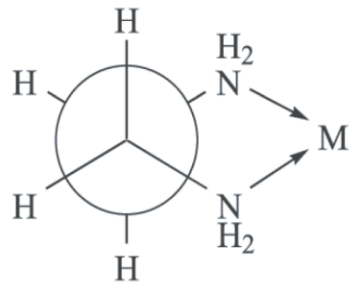






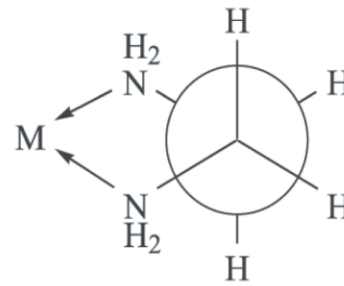
**Ethylenediamine (en)
ligand attached to M**





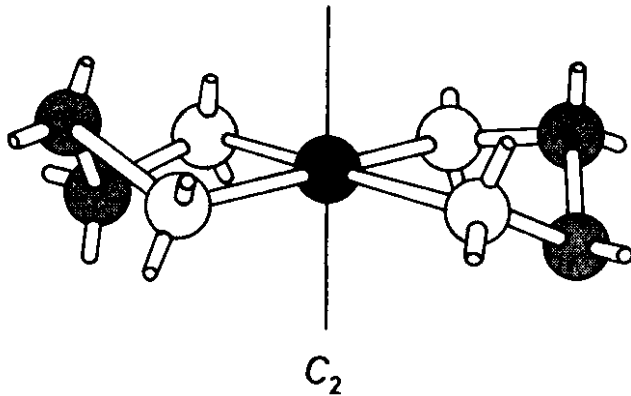
δ

Mirror plane



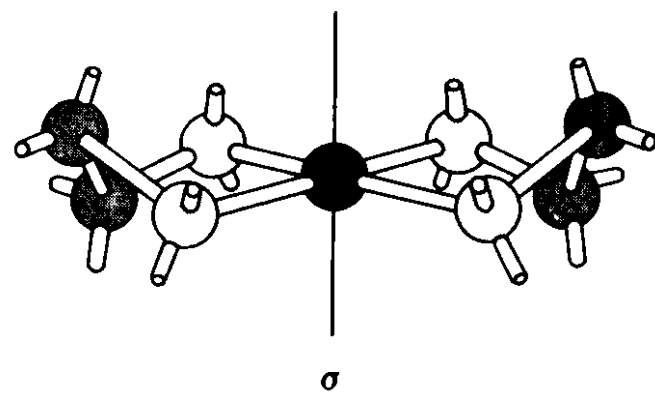
λ

(A) = $\lambda\lambda$

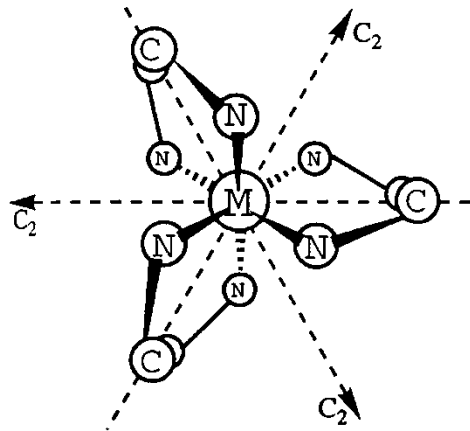


enantiomeri $\lambda\lambda$ e $\delta\delta$

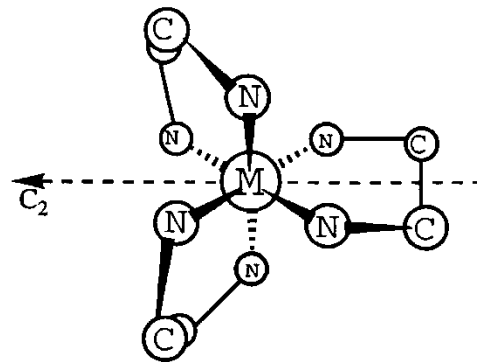
(B) = $\lambda\delta$



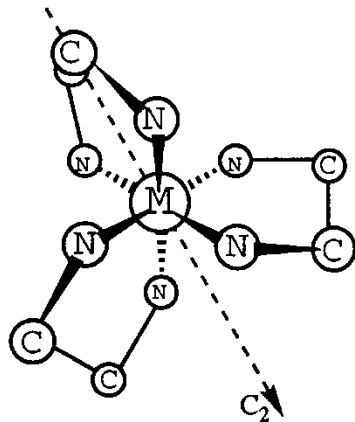
meso $\lambda\delta$



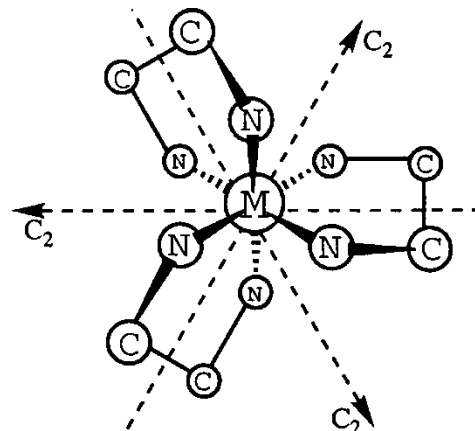
(a) $\Lambda(\delta, \delta, \delta)$
 D_3



(b) $\Lambda(\delta, \delta, \lambda)$
 C_2



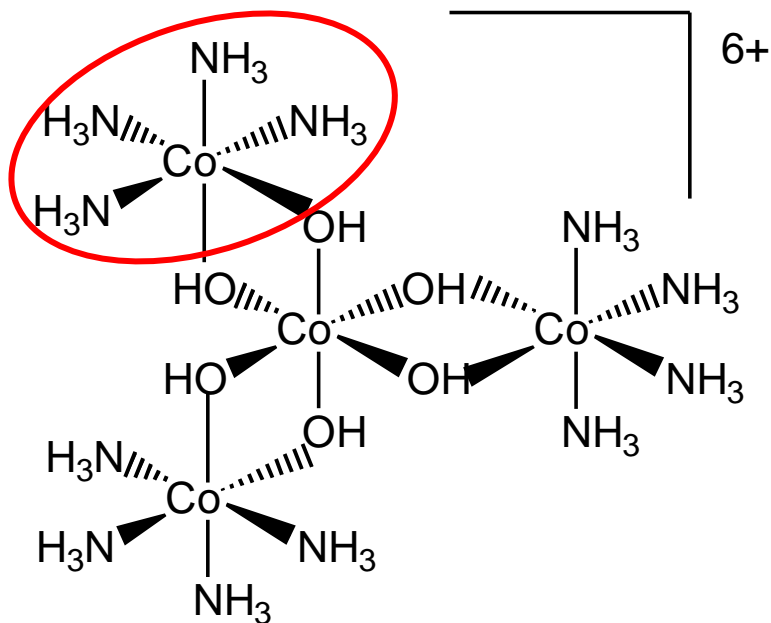
(c) $\Lambda(\delta, \lambda, \lambda)$
 C_2



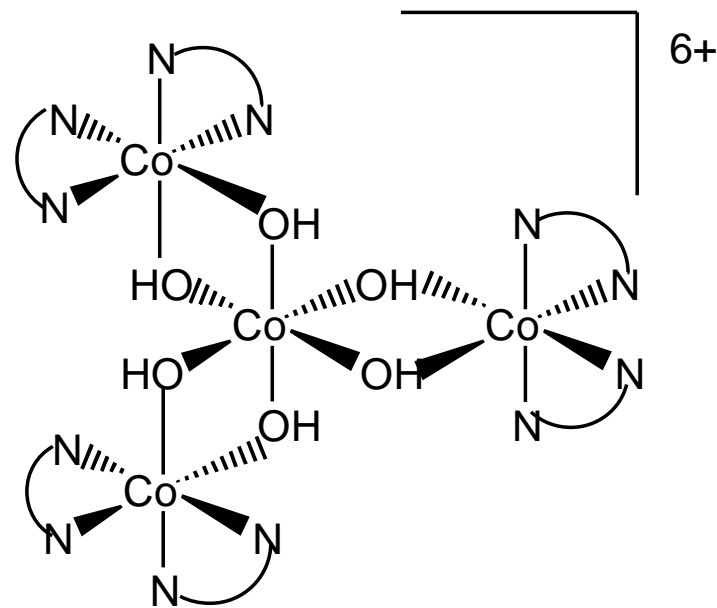
(d) $\Lambda(\lambda, \lambda, \lambda)$
 D_3

208 ($\lambda e \delta$)

2912 ($R e S$)



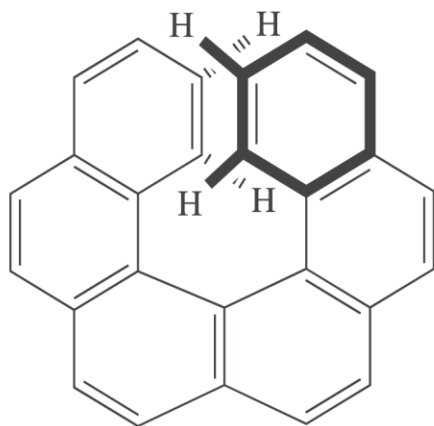
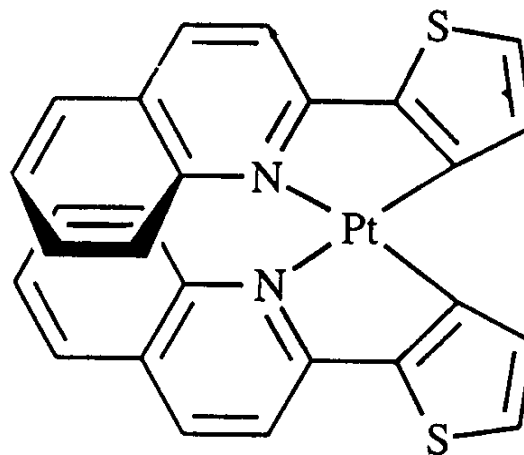
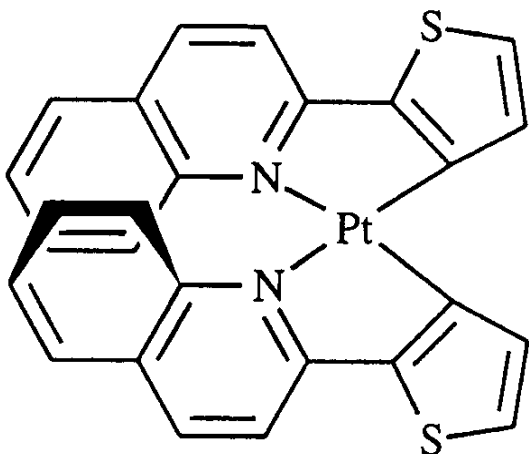
$\Lambda e \Delta$



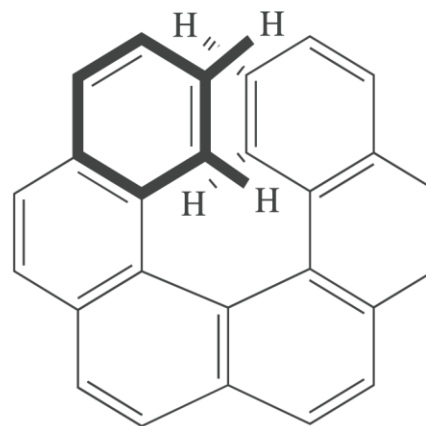
$\Delta(\Delta)_3$	$\Lambda(\Lambda)_3$
$\Delta\{(\Delta)_2\Lambda\}$	$\Lambda\{(\Lambda)_2\Delta\}$
$\Delta\{\Delta(\Lambda)_2\}$	$\Lambda\{\Lambda(\Delta)_2\}$
$\Delta(\Lambda)_3$	$\Lambda(\Delta)_3$

$\Delta(S)_6, \Delta(S)_5(R), \Delta(S)_4(R)_2, \Delta(S)_3(R)_3, \dots$

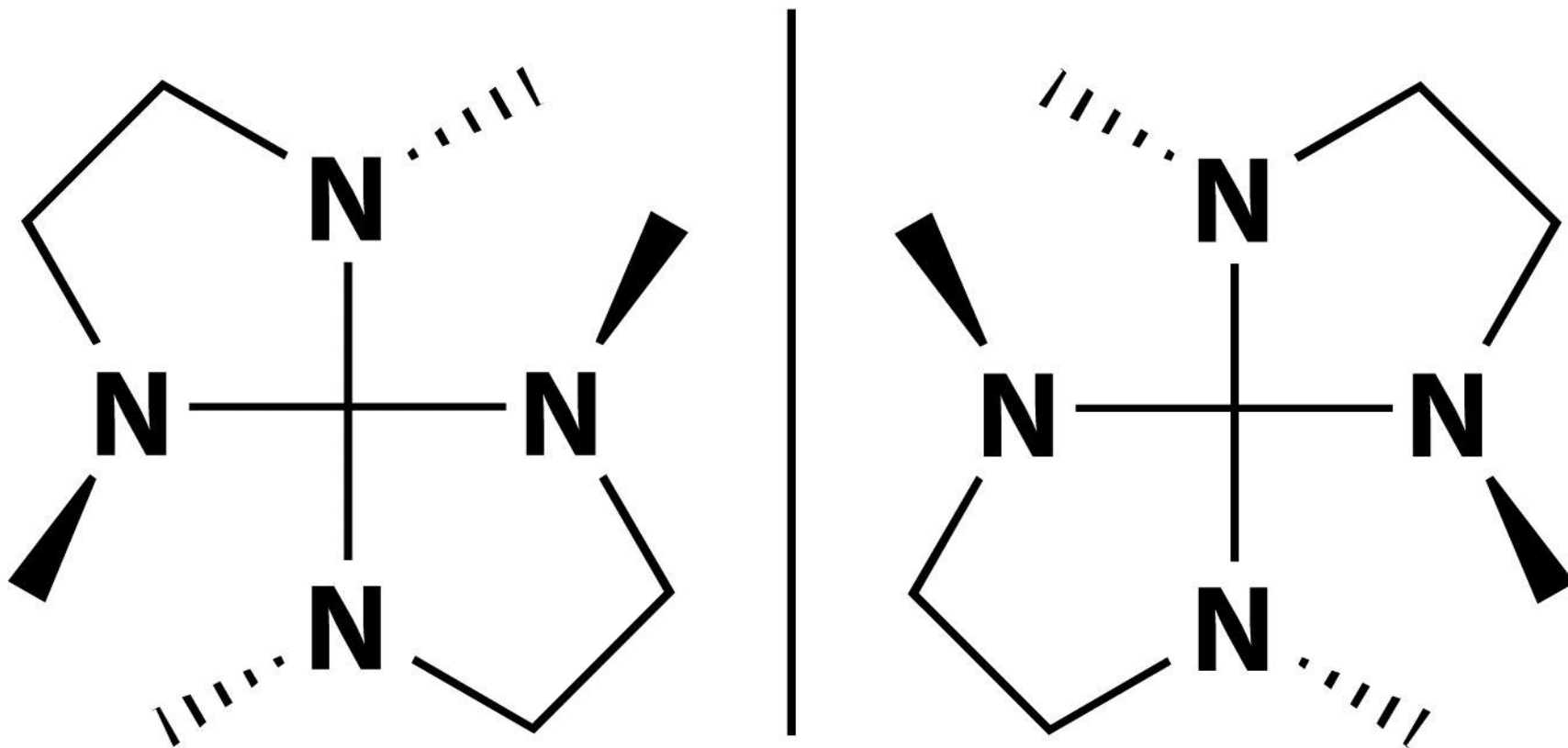
Chiralità nei complessi planari quadrati



(P)-hexahelicene

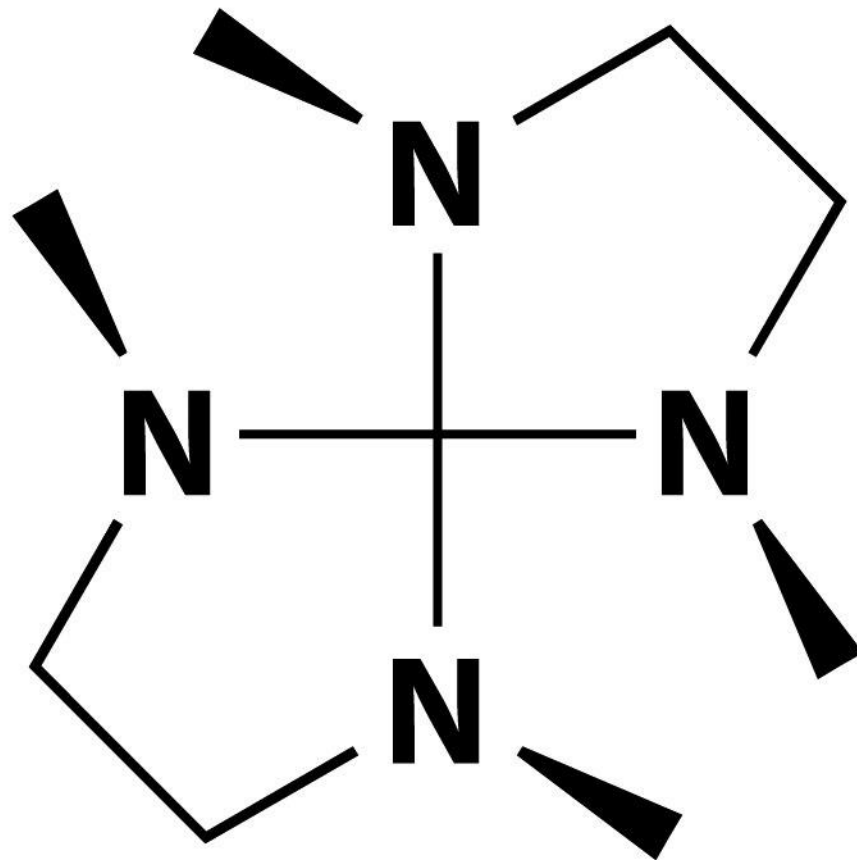


(M)-hexahelicene



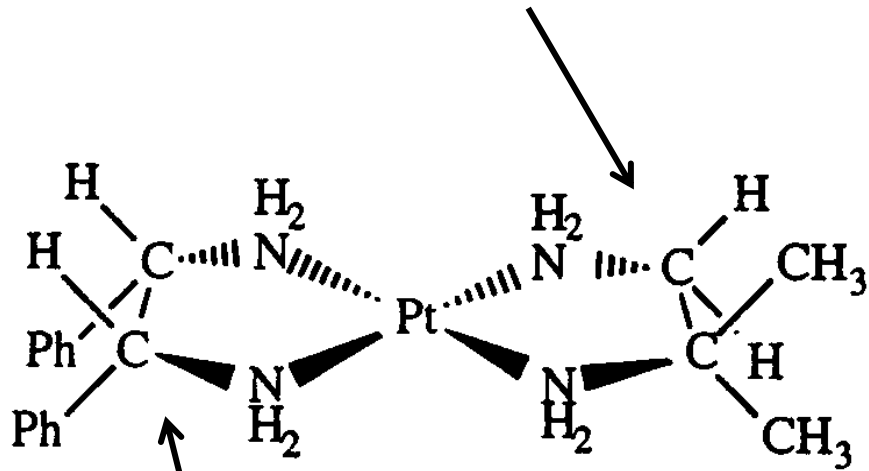
racemo

N diventa chirale in seguito alla coordinazione

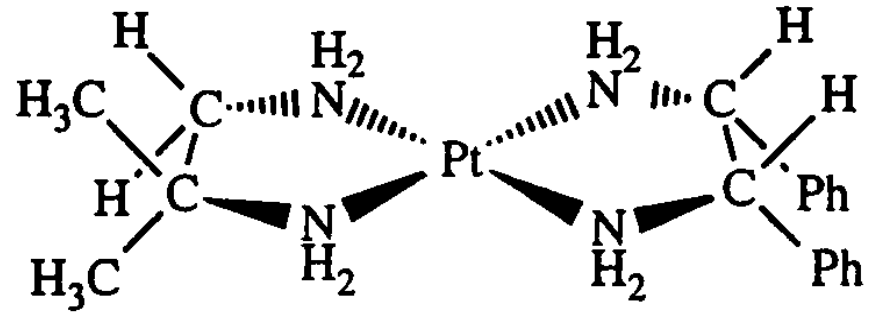


meso

isobutilene-diammina



meso-stilbenediammina



in seguito alla coordinazione, la simmetria che rende ciascun legante achirale viene persa