

## Isomerism in coordination complexes

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graph TD; A[Isomerism in coordination complexes] --> B[Structural isomerism]; A --> C[Stereoisomerism]; B --> D[Ionization isomerism]; B --> E[Hydration isomerism]; B --> F[Coordination isomerism]; B --> G[Linkage isomerism]; C --> H[Diastereoisomers]; C --> I[Enantiomers];
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### Structural isomerism

Ionization isomerism  
Hydration isomerism  
Coordination isomerism  
Linkage isomerism

### Stereoisomerism

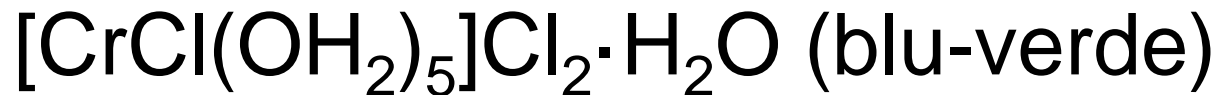
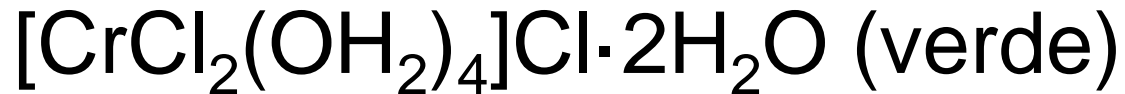
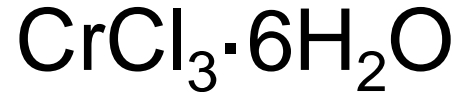
Diastereoisomers  
Enantiomers

# Isomeri di ionizzazione

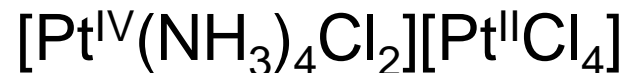
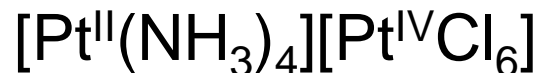
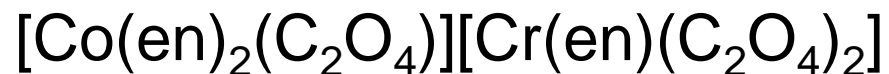
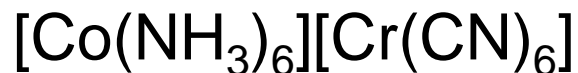
$[\text{CoCl}_2(\text{en})_2]\text{NO}_2$  (verde)  
 $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{SO}_4)$  (violetto)

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

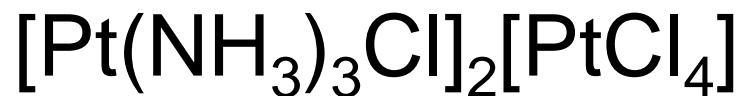
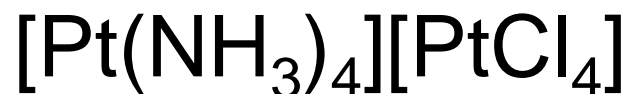
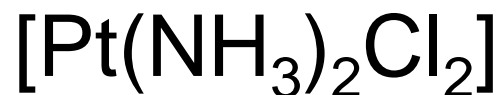
# Isomeri di idratazione



# Isomeri di coordinazione



# Isomeri di polimerizzazione



# Isomeri di legame (leganti ambidentati)

–NO<sub>2</sub> (nitro)

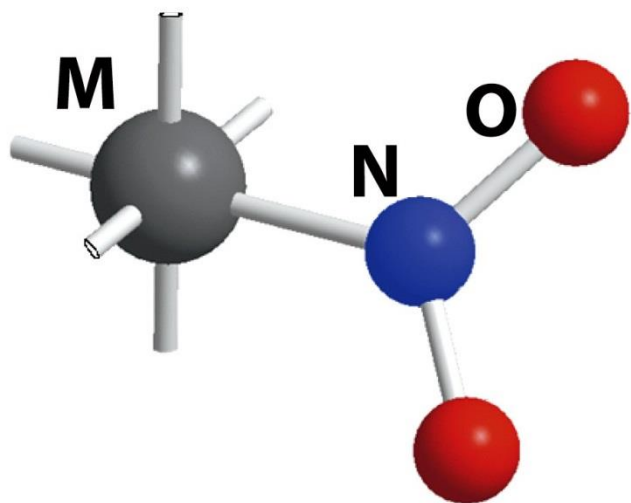
–C≡N (nitrile)

–S–C≡N<sup>–</sup> (tiocianato)

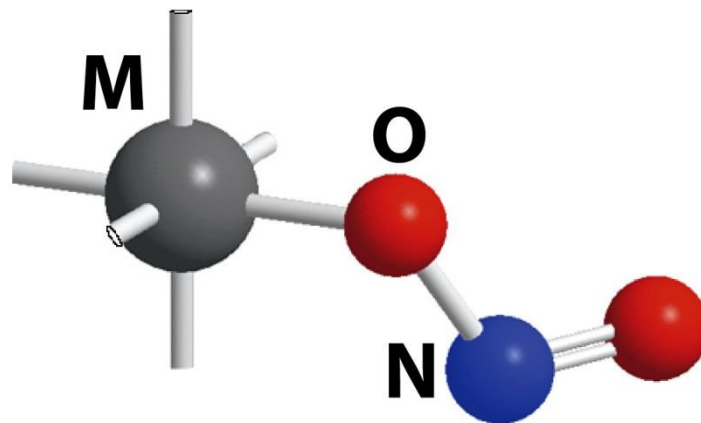
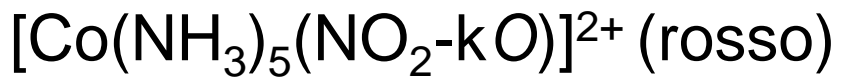
–O–NO (nitrito)

–N≡C (isonitrile)

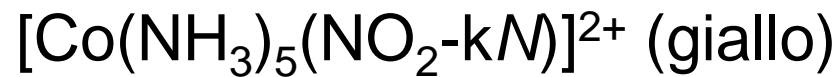
–N=C=S<sup>–</sup> (isotiocianato)

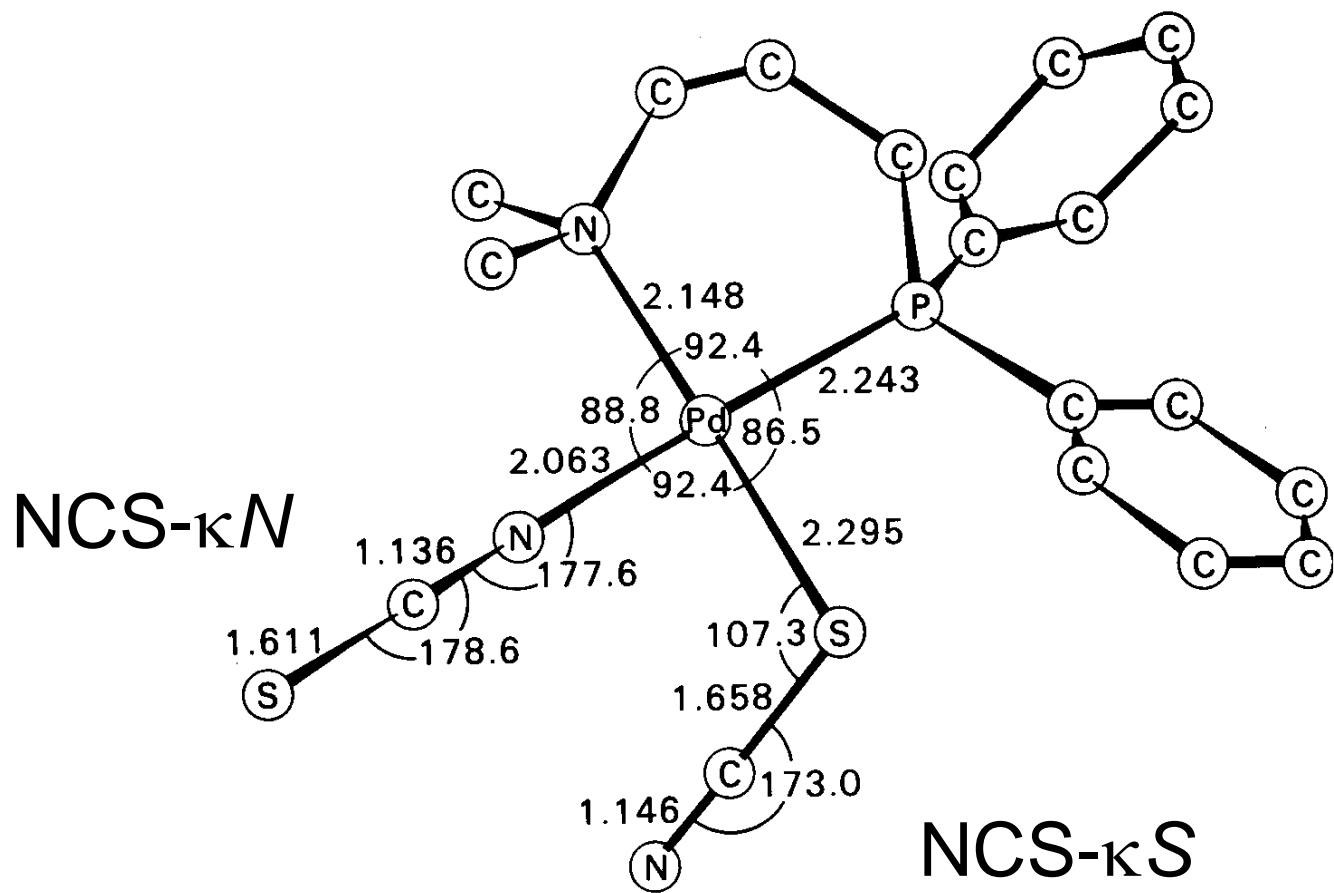


**Nitro ligand**

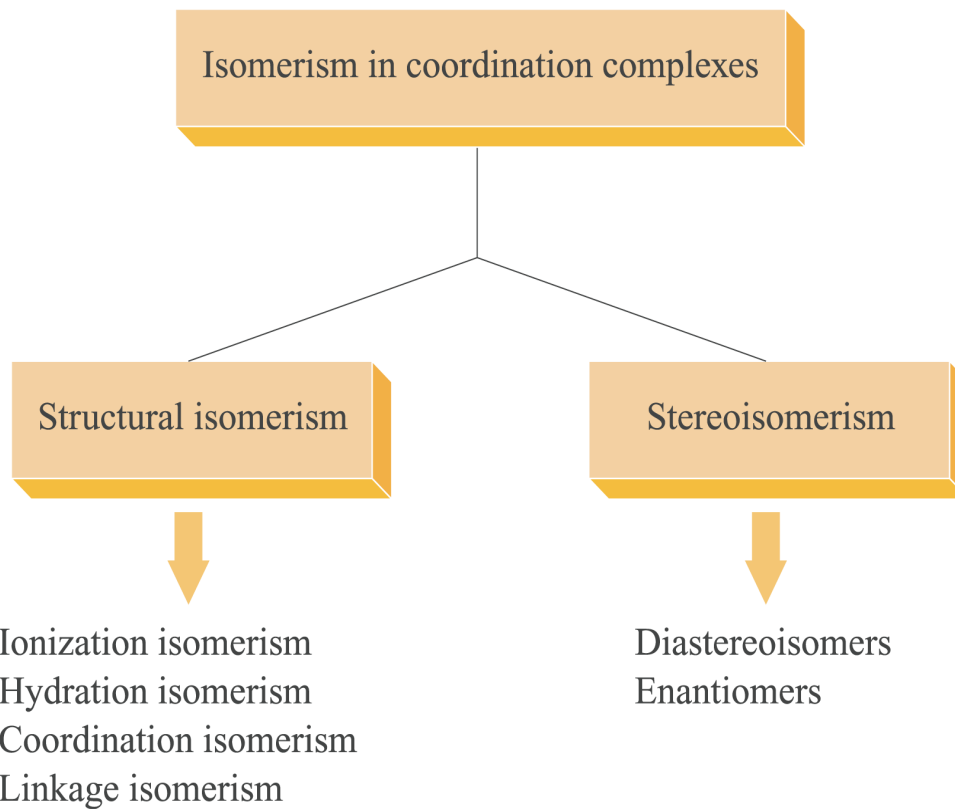


**Nitrito ligand**

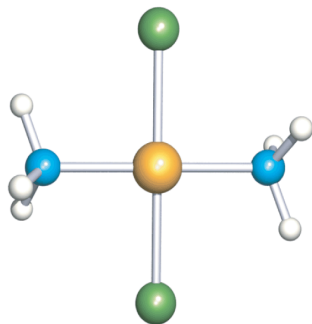




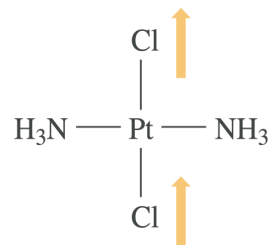




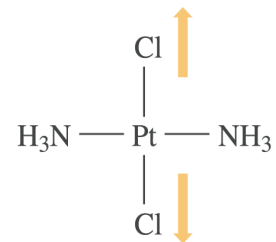
*stereoisomeri che non siano enantiomeri sono diastereoisomeri*



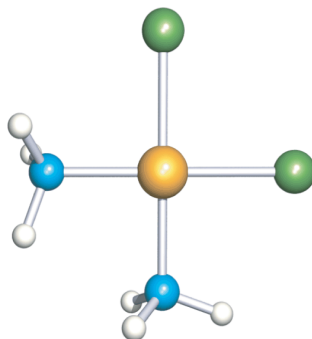
The *trans*-isomer is non-polar



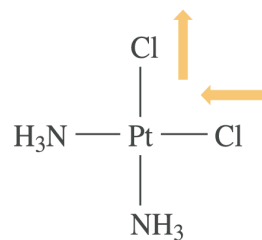
Asymmetric stretch:  
IR active  
 $365\text{ cm}^{-1}$



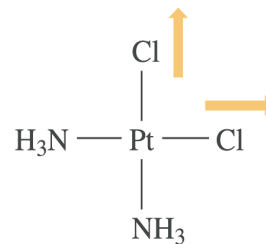
Symmetric stretch:  
IR inactive



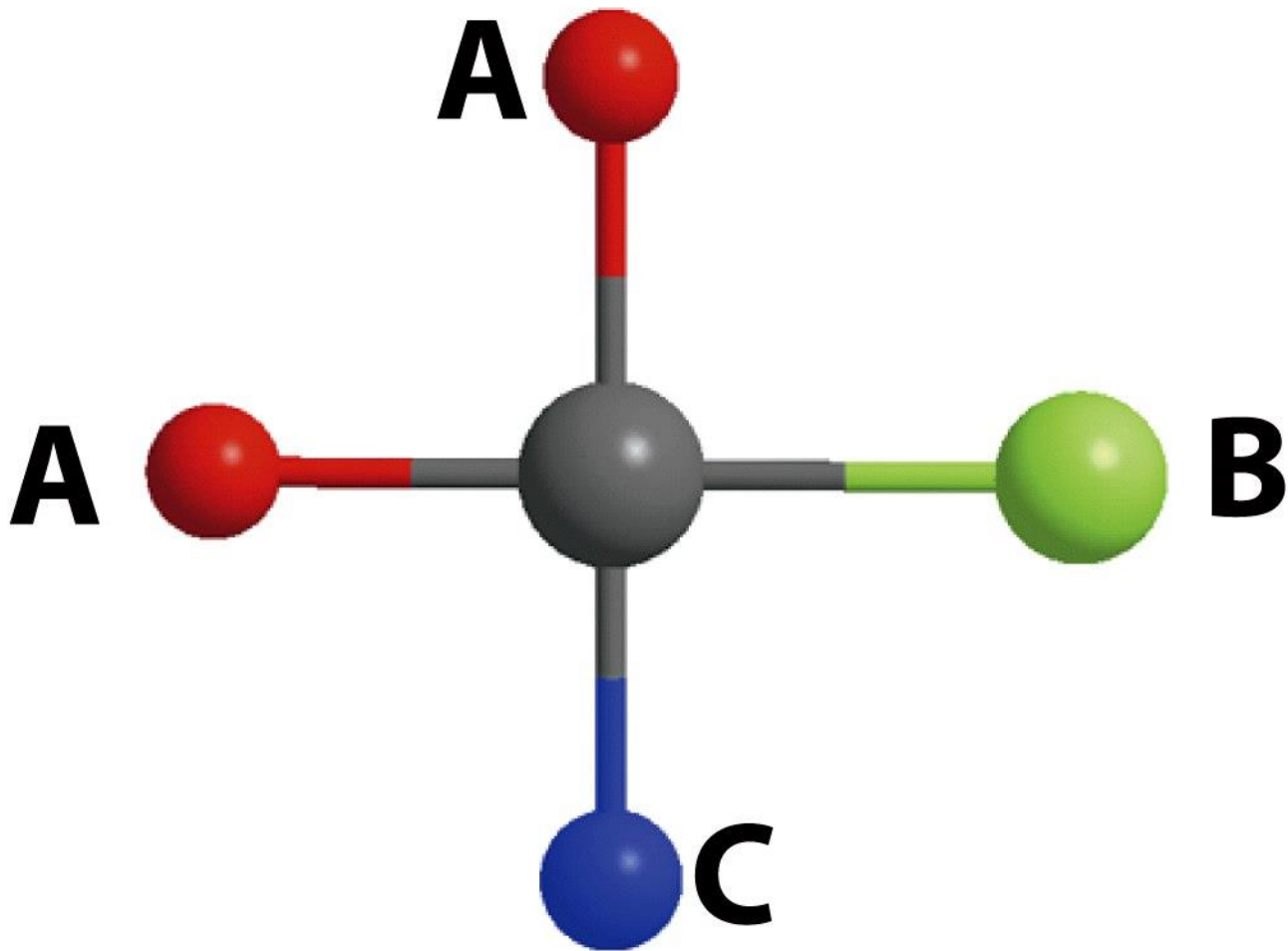
The *cis*-isomer is polar



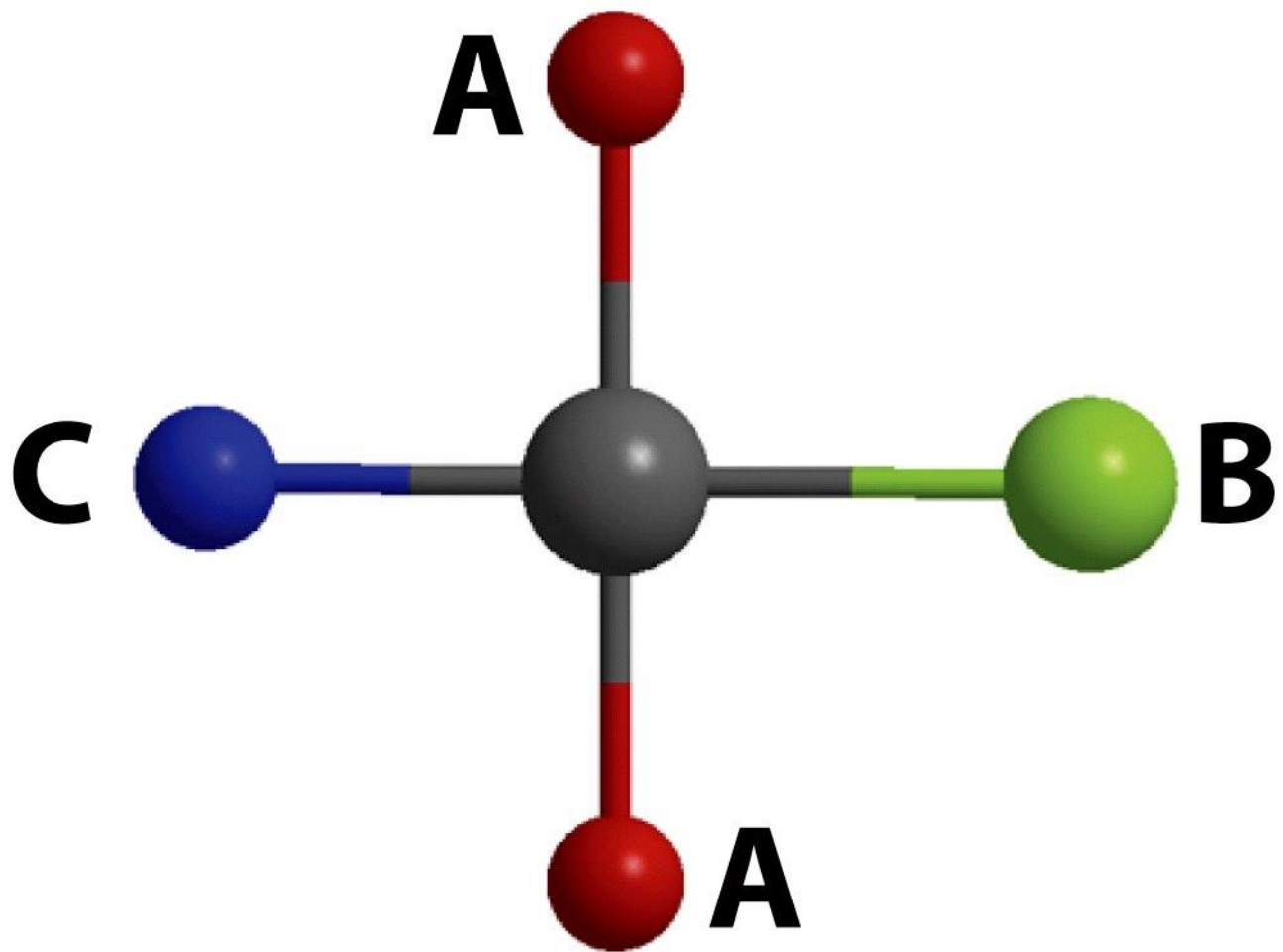
Asymmetric stretch:  
IR active  
 $330\text{ cm}^{-1}$



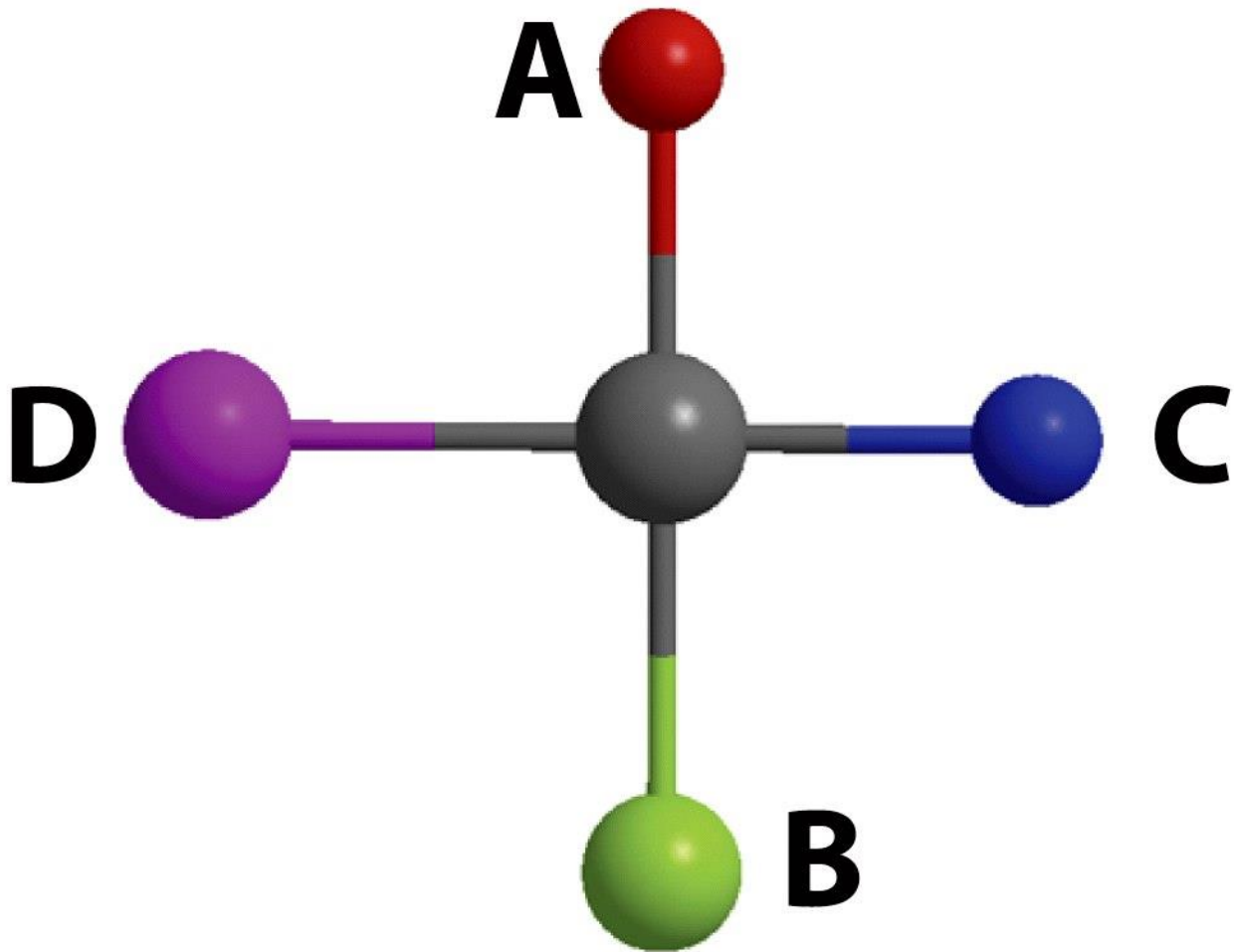
Symmetric stretch:  
IR active  
 $323\text{ cm}^{-1}$



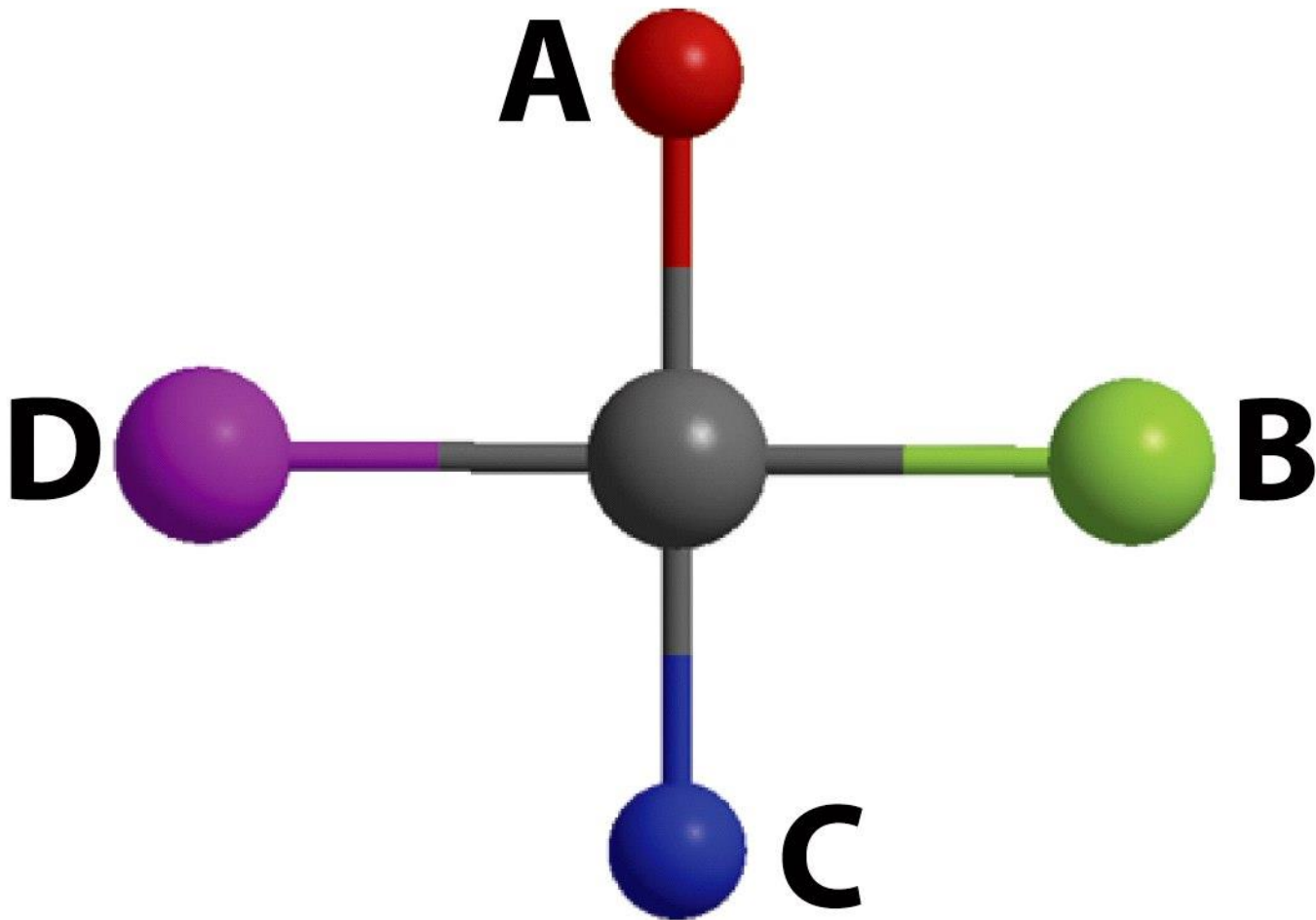
***cis*-[MA<sub>2</sub>BC]**



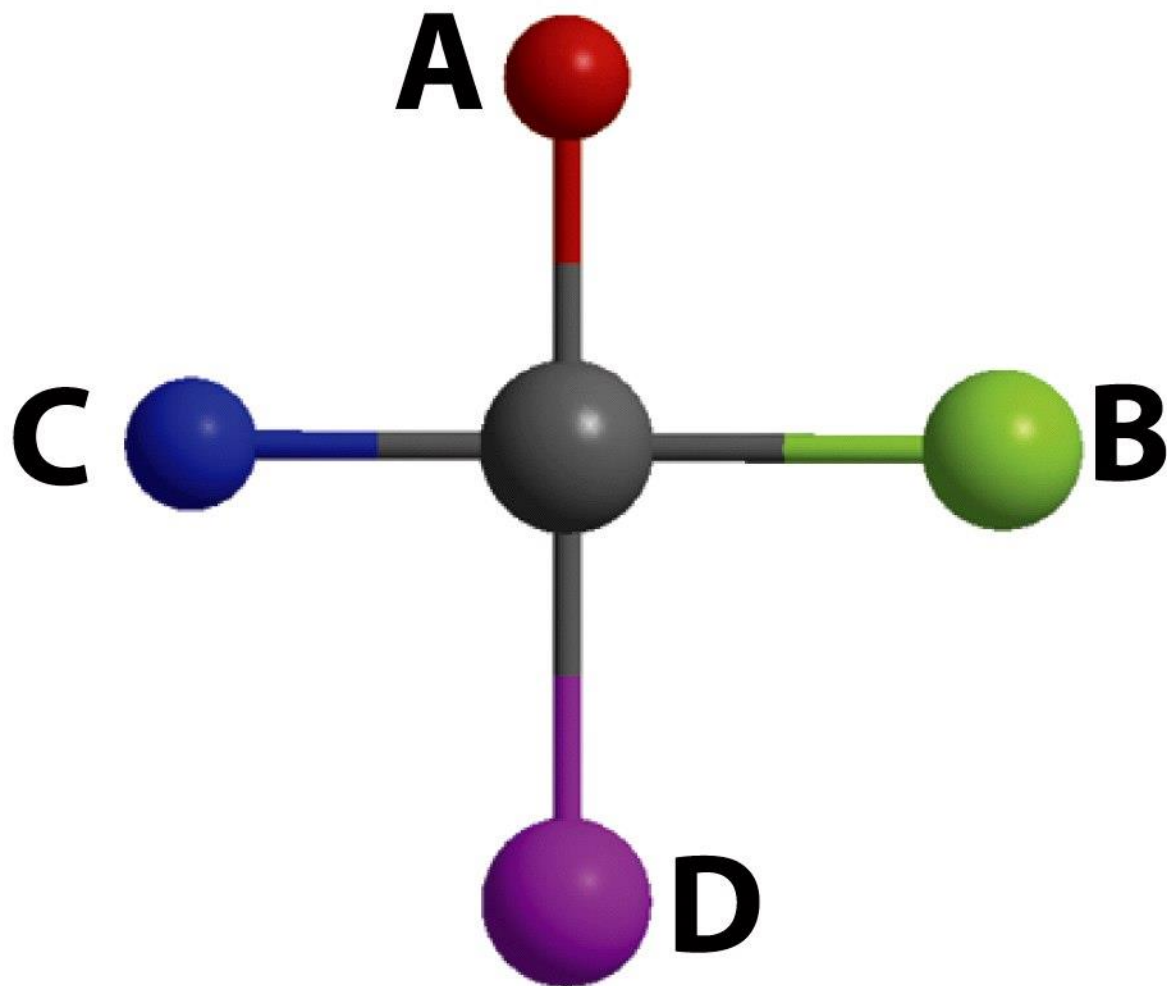
***trans*-[MA<sub>2</sub>BC]**



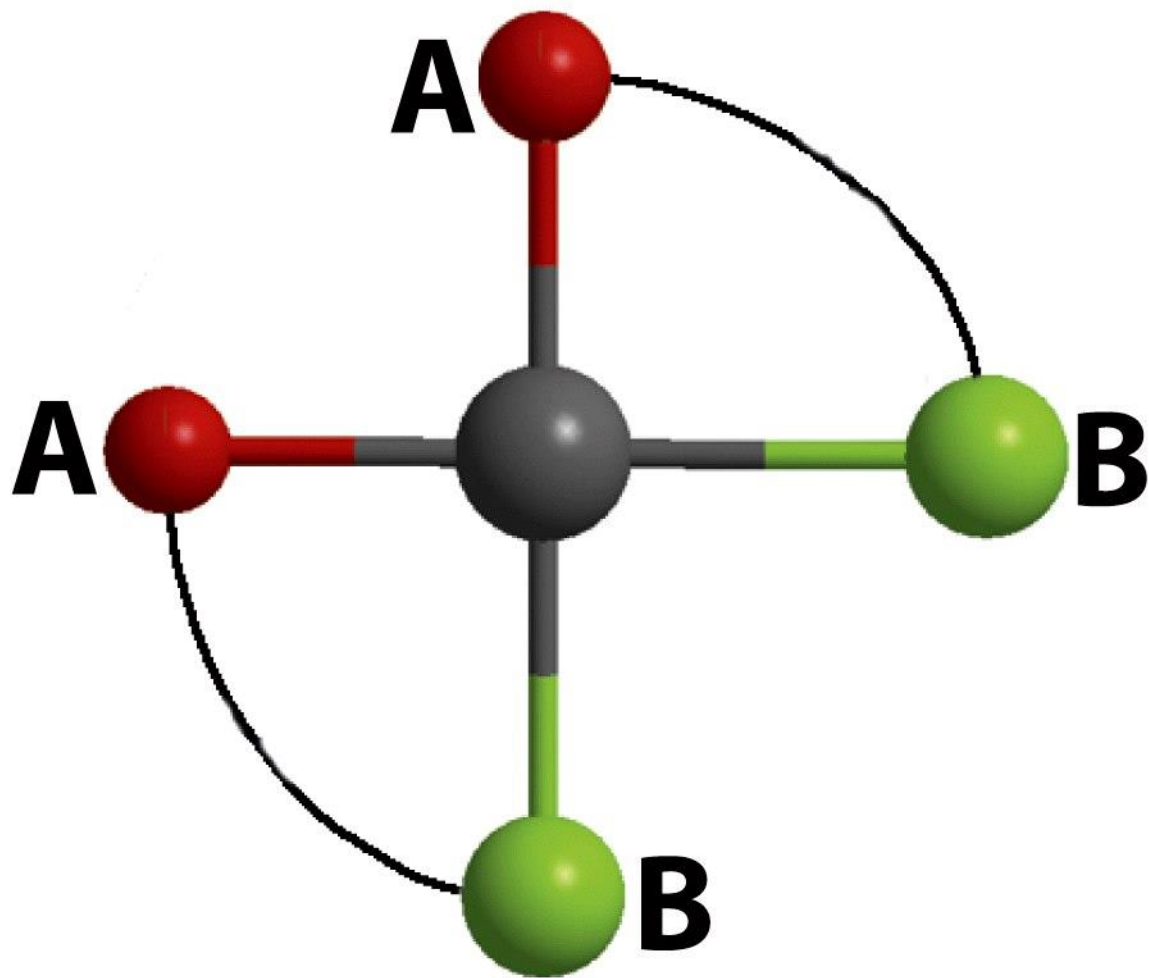
**[MABCD], A *trans* to B**



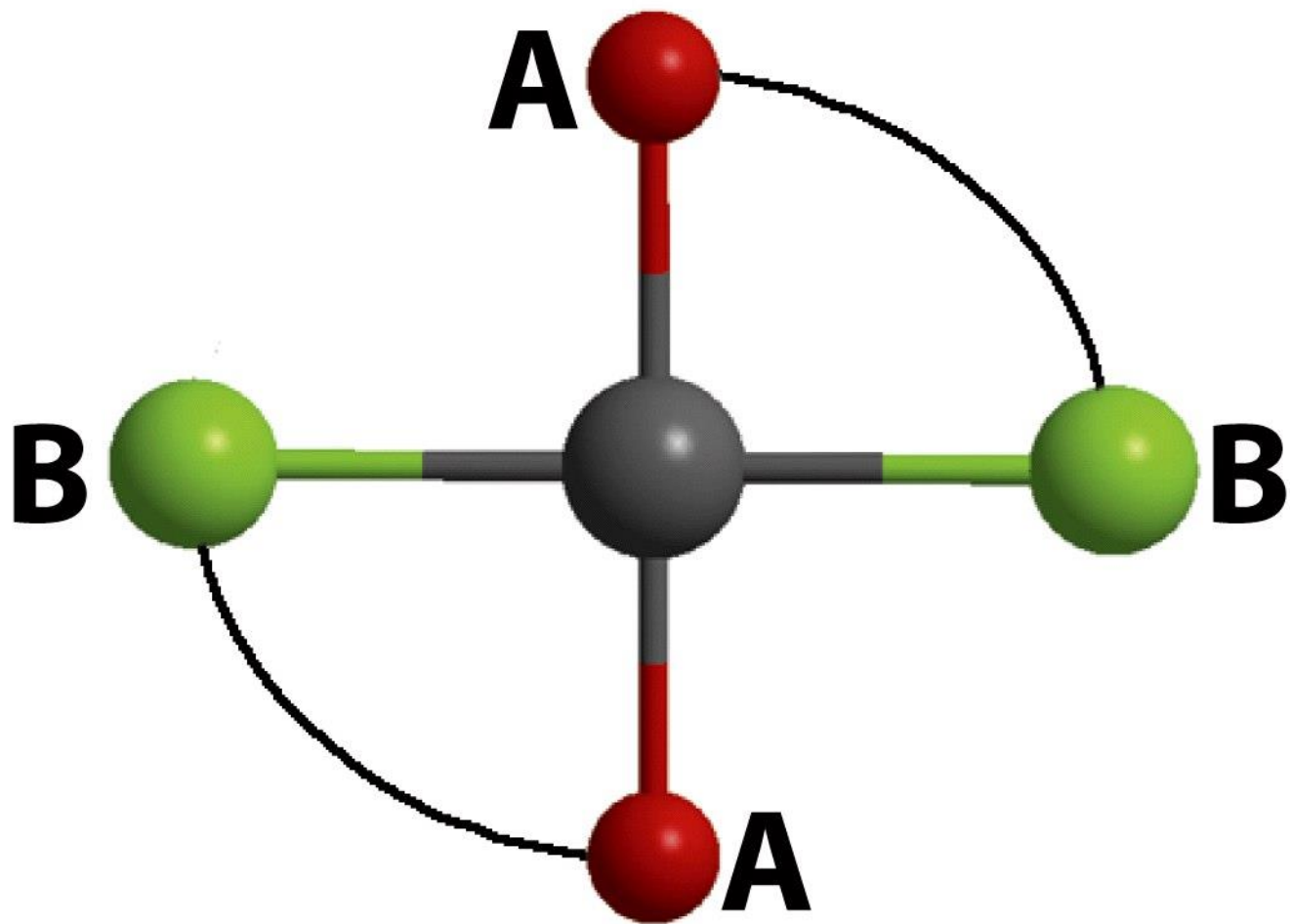
**[MABCD], *A trans to C***

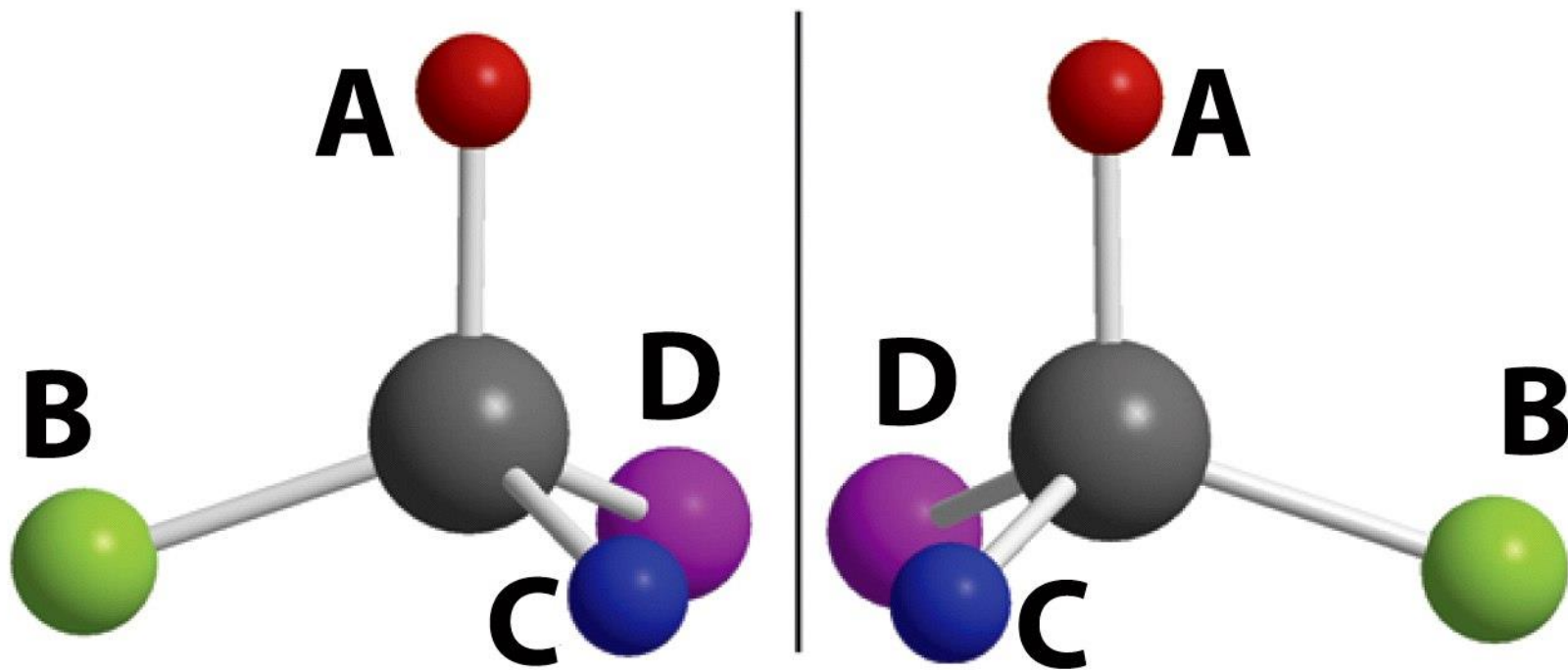


**[MABCD], A *trans* to D**

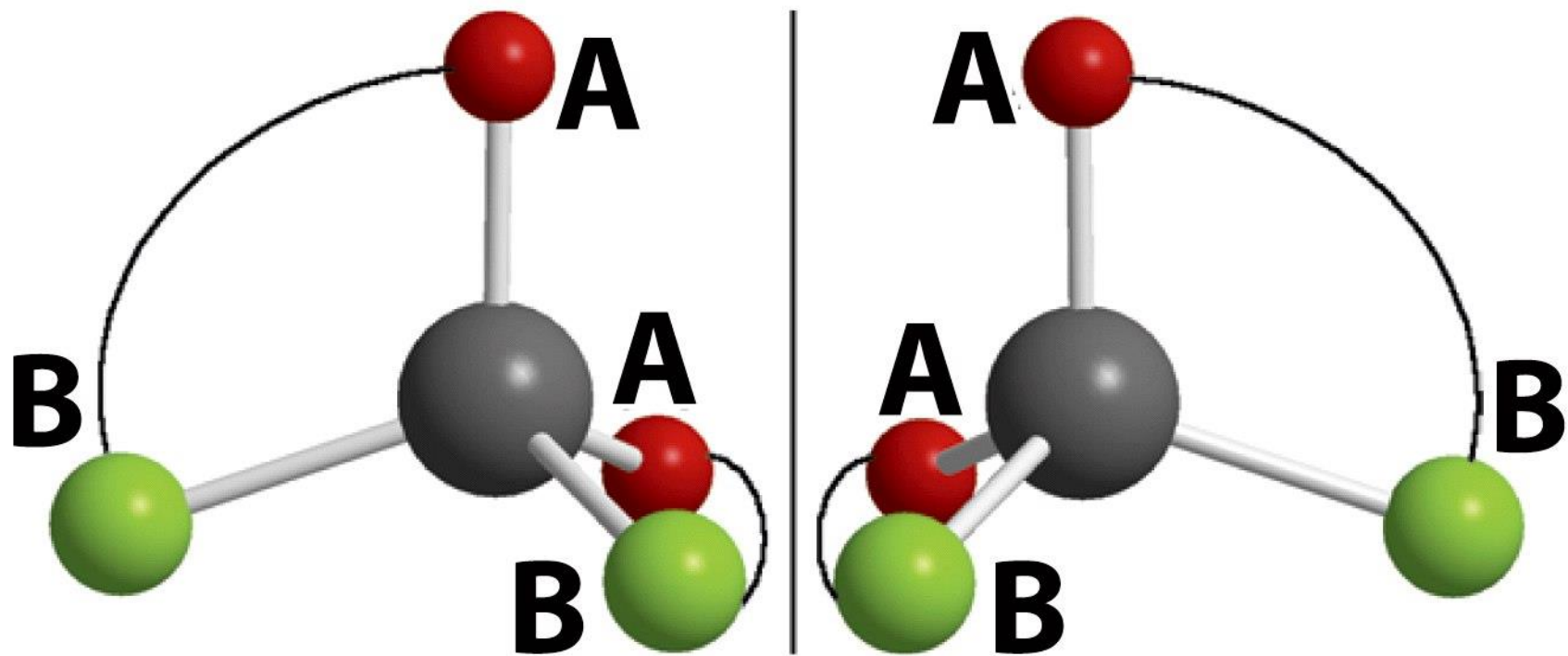




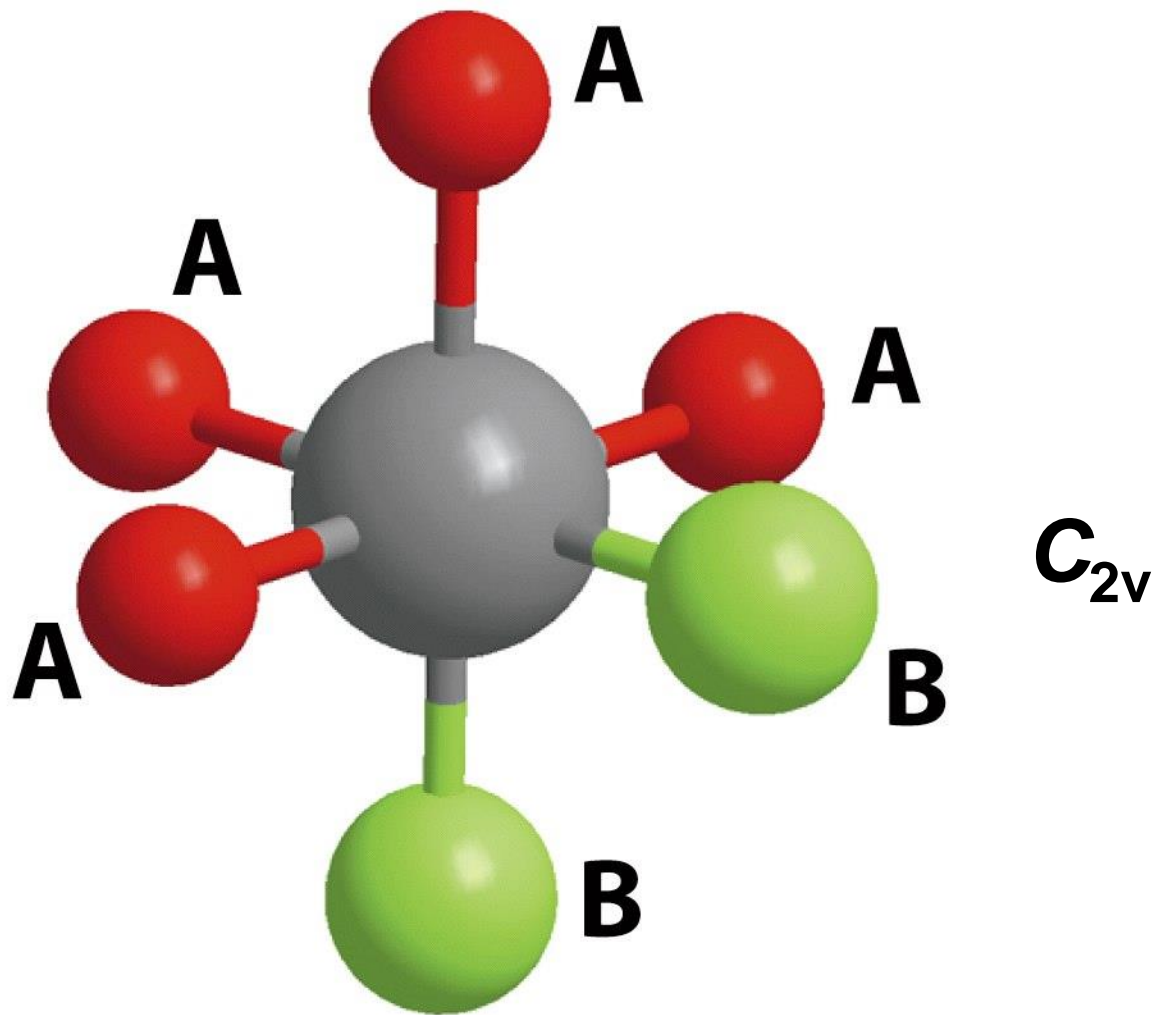


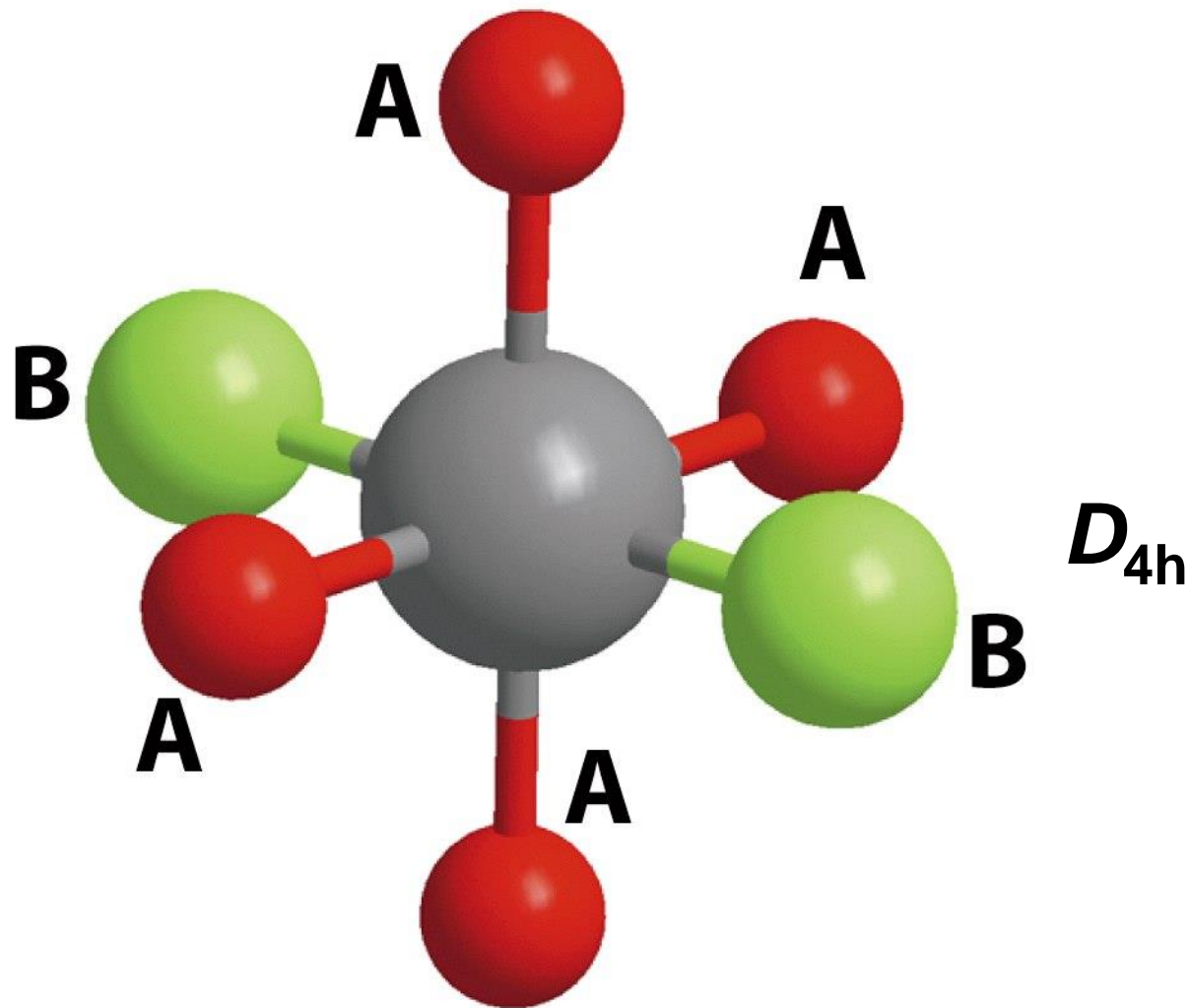


**[MABCD] enantiomers**

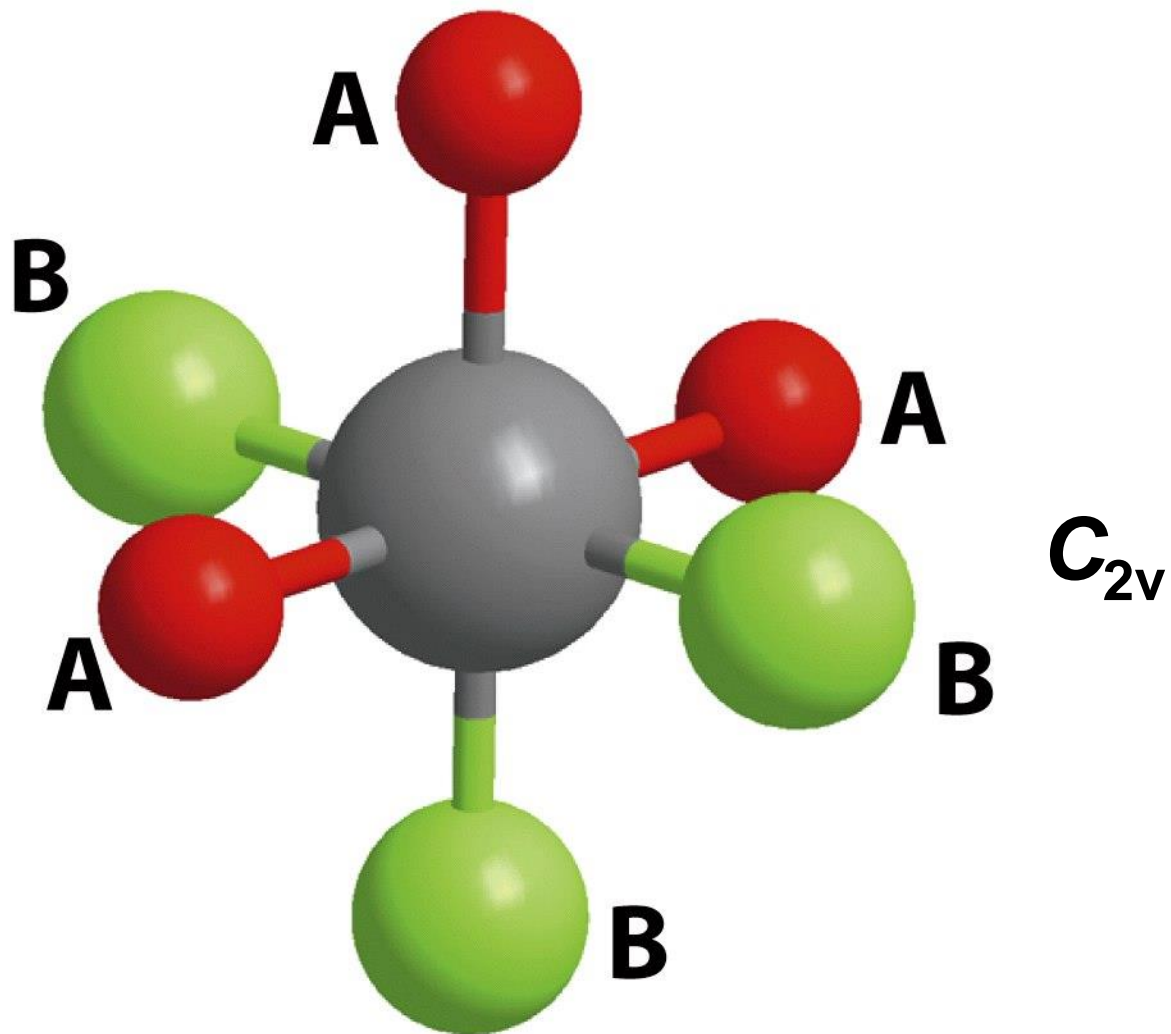


**$[M(AB)_2]$  enantiomers**

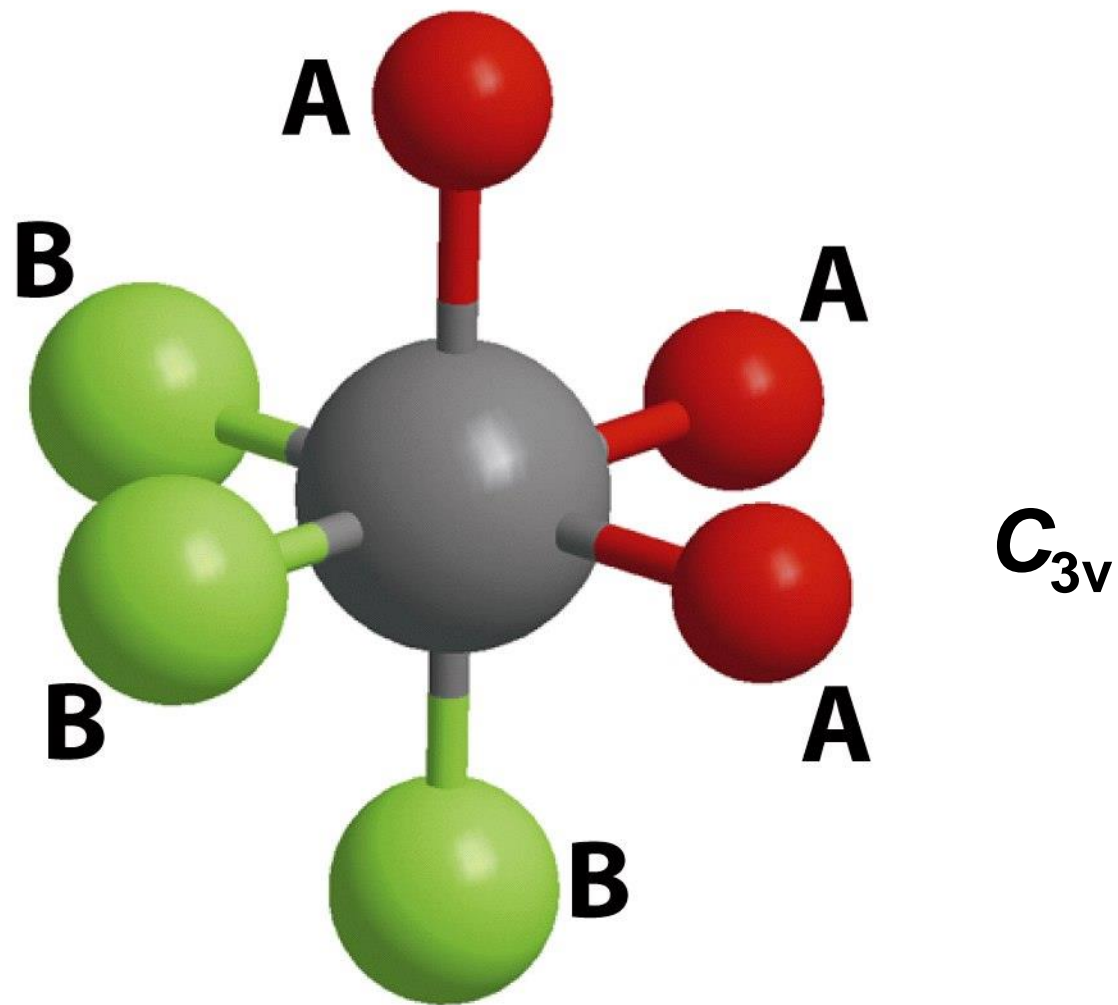




***trans*-[MA<sub>4</sub>B<sub>2</sub>]**

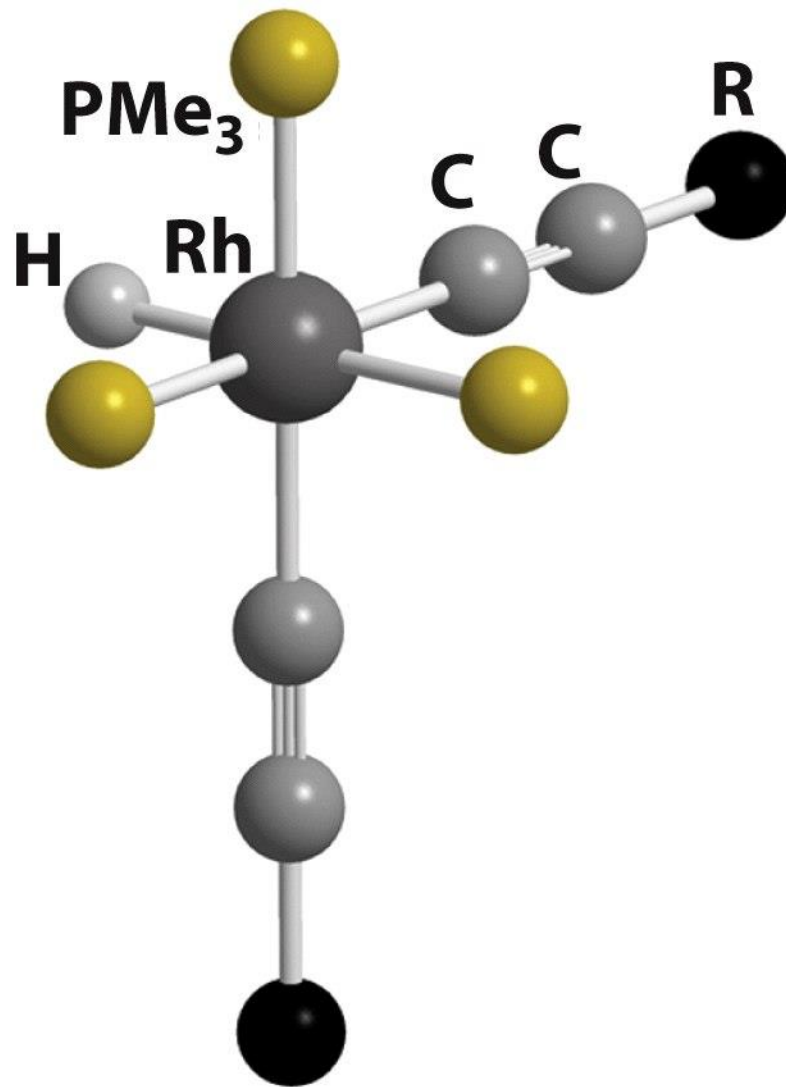


*meridional*

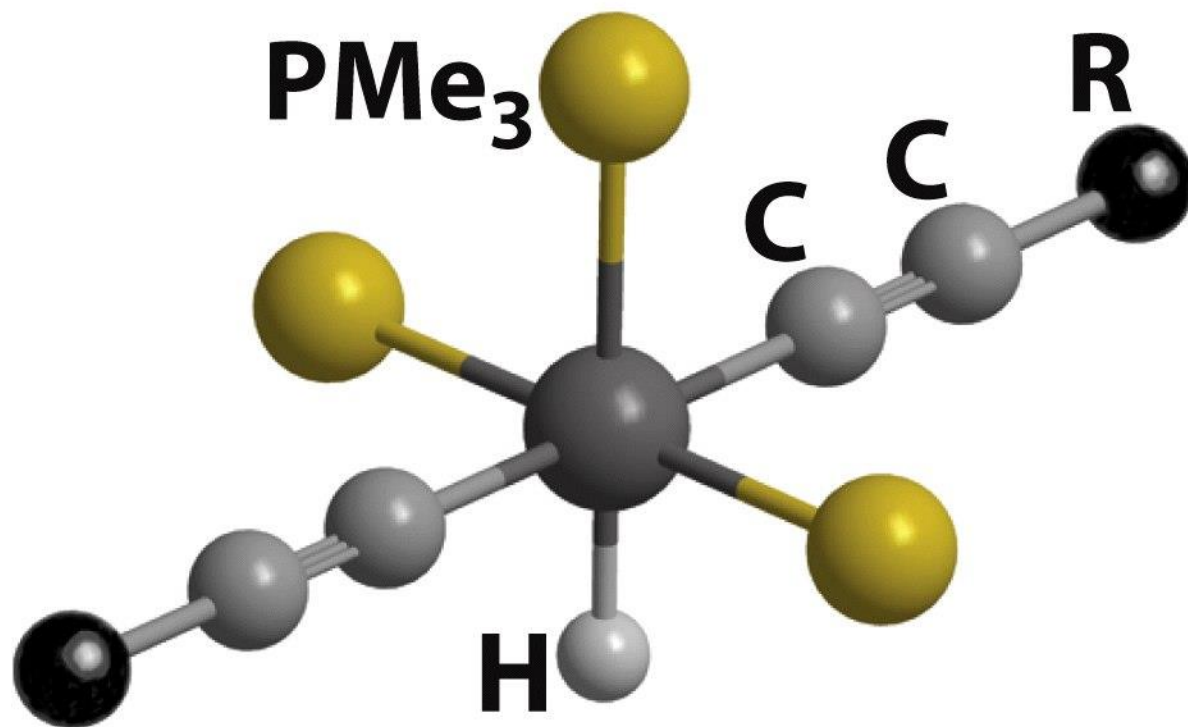


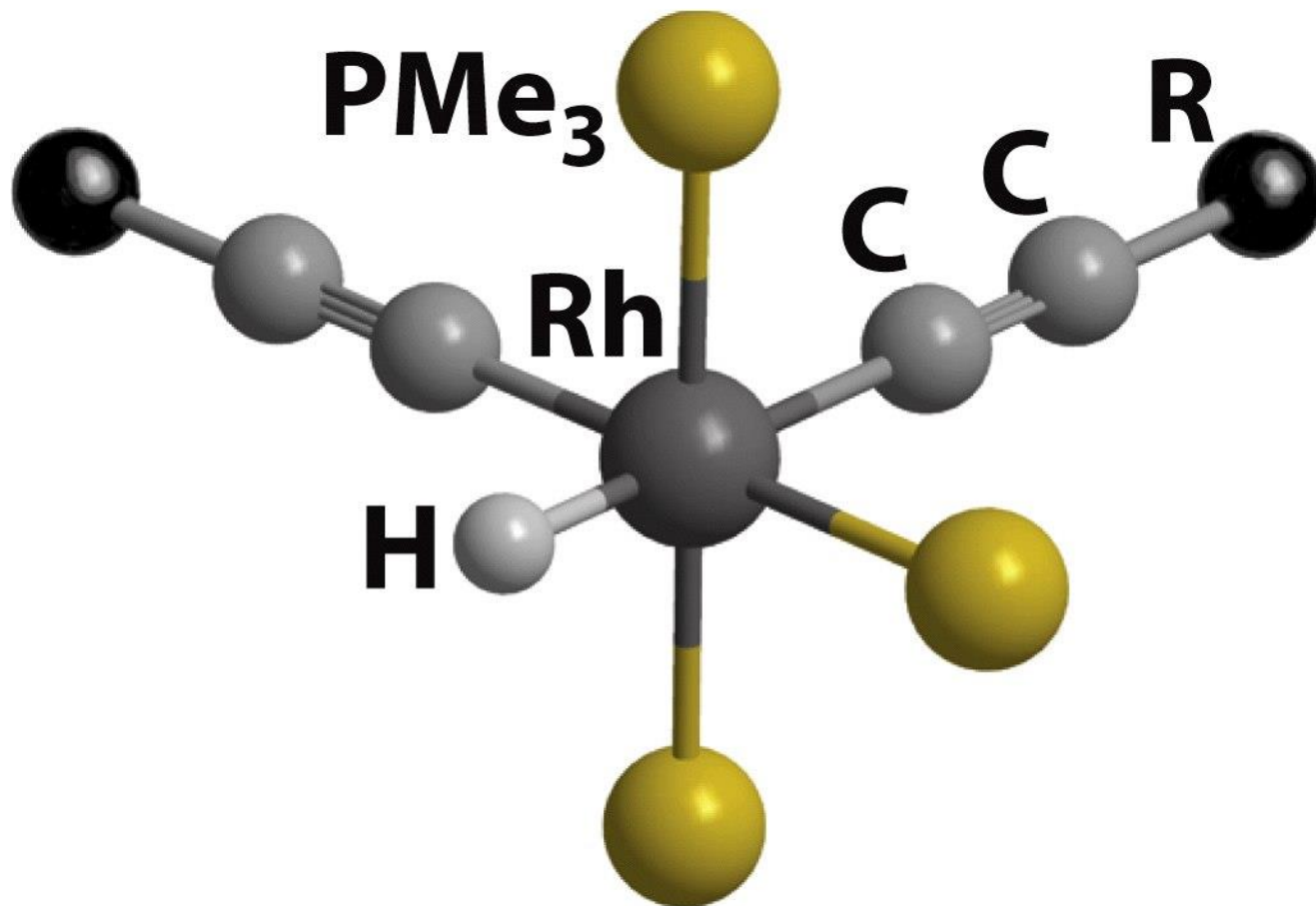
***fac***-[MA<sub>3</sub>B<sub>3</sub>]

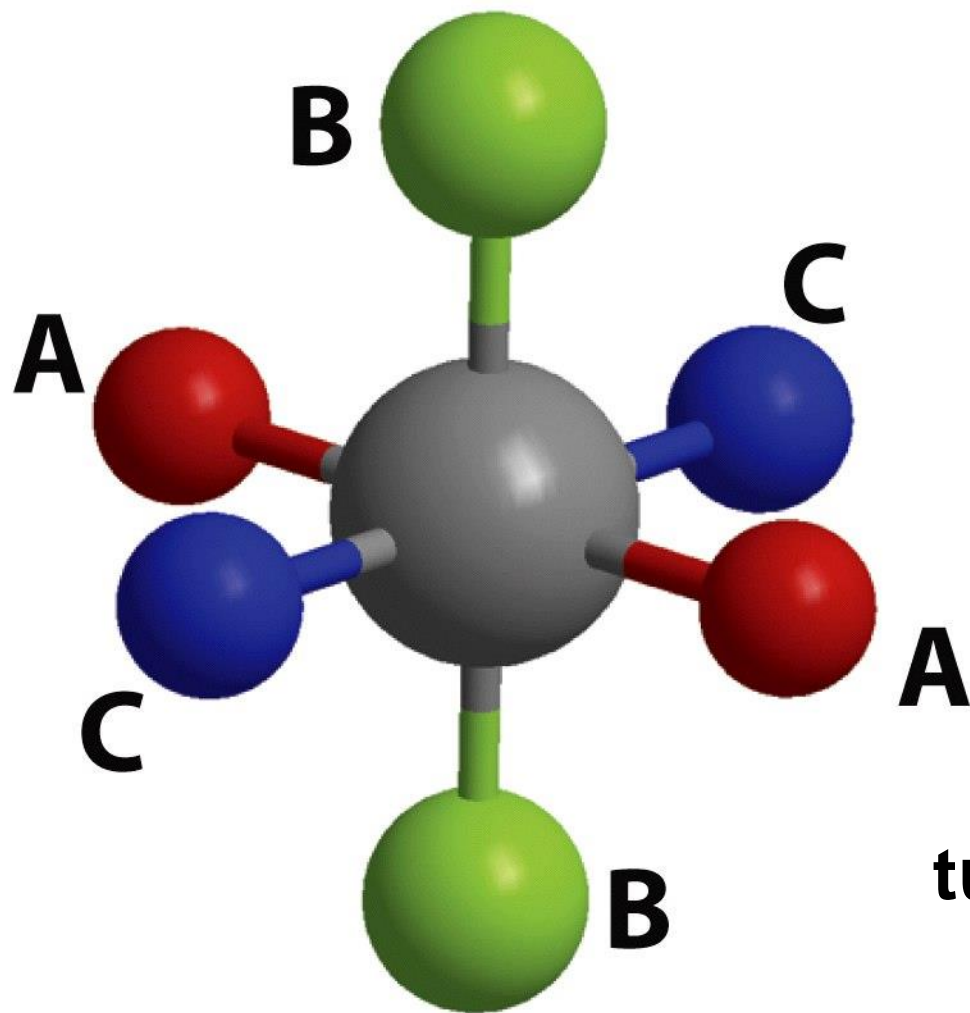
*facial*





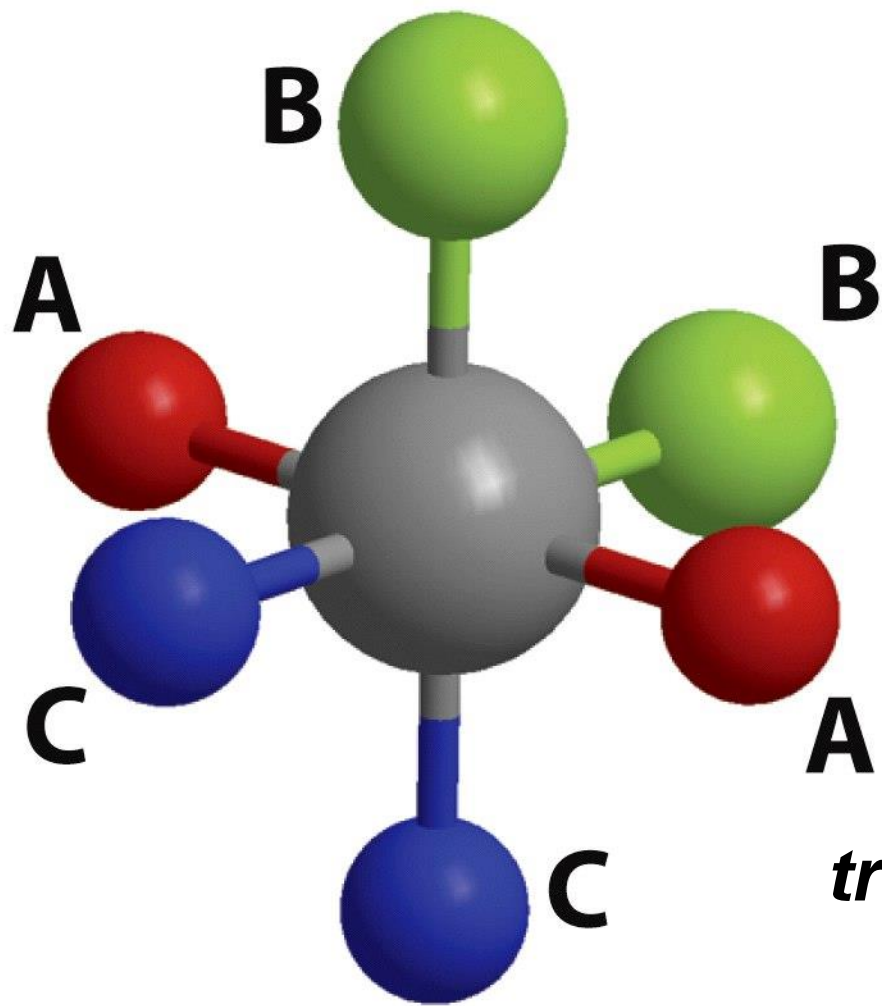






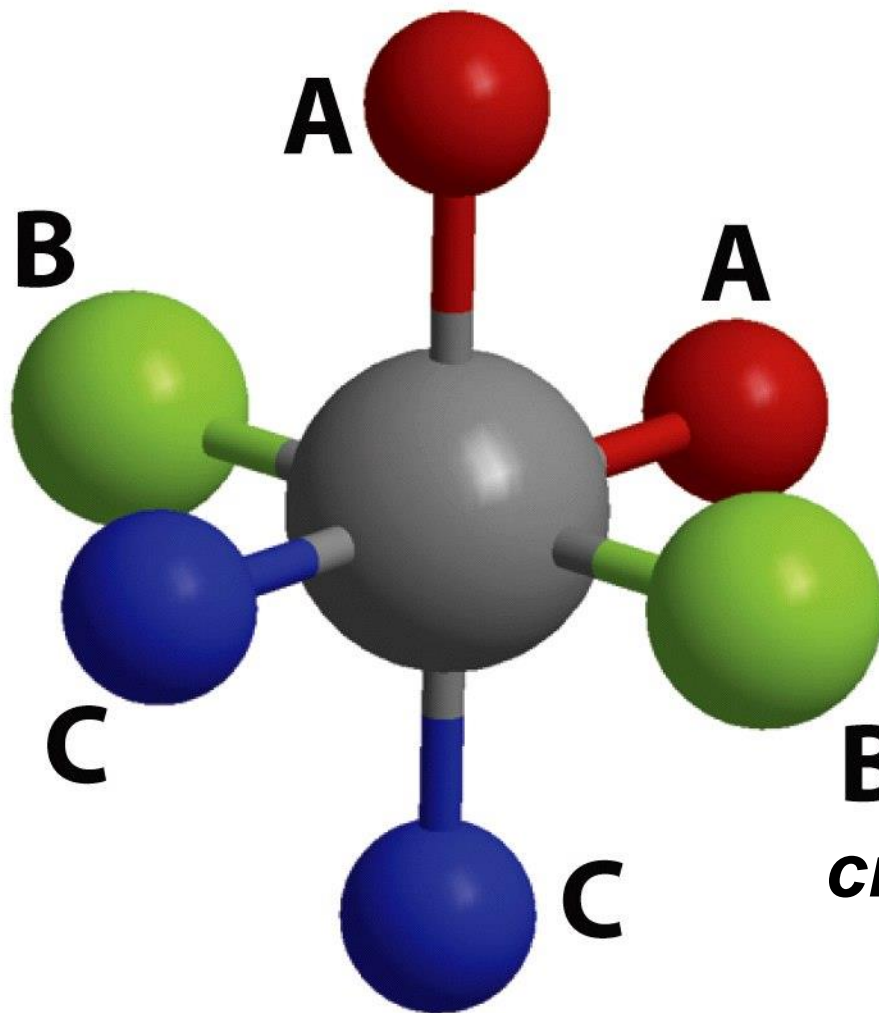
*tutto-trans*





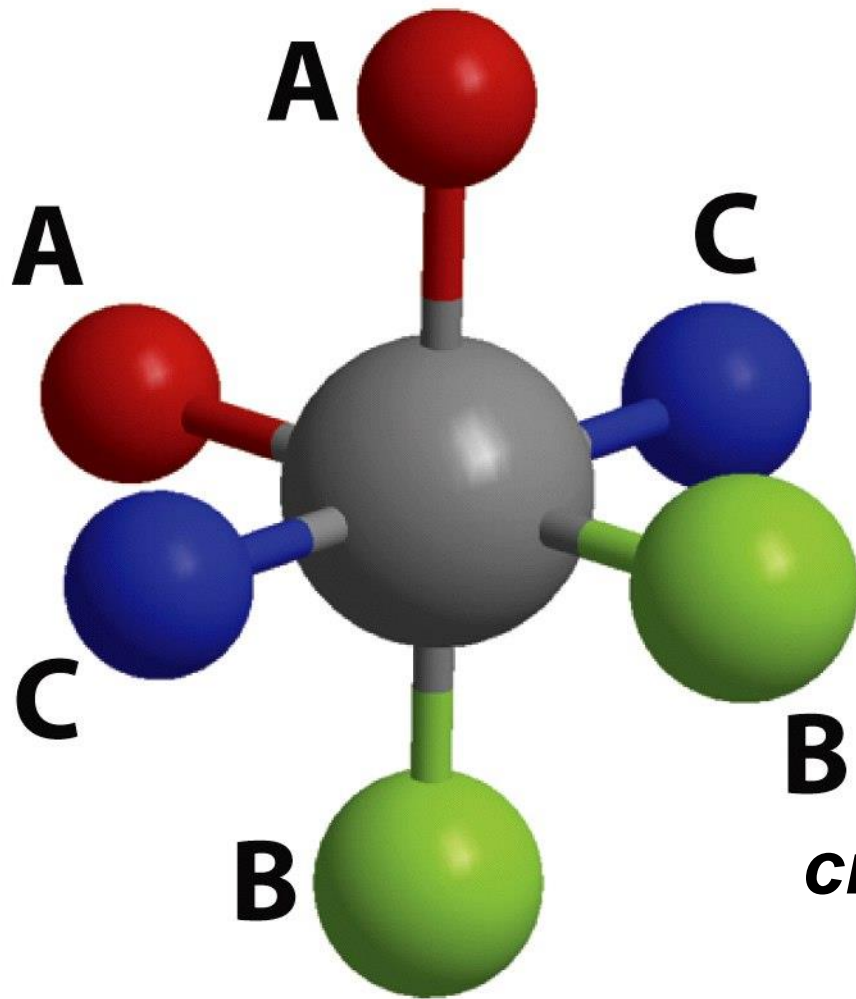
*trans, cis, cis*





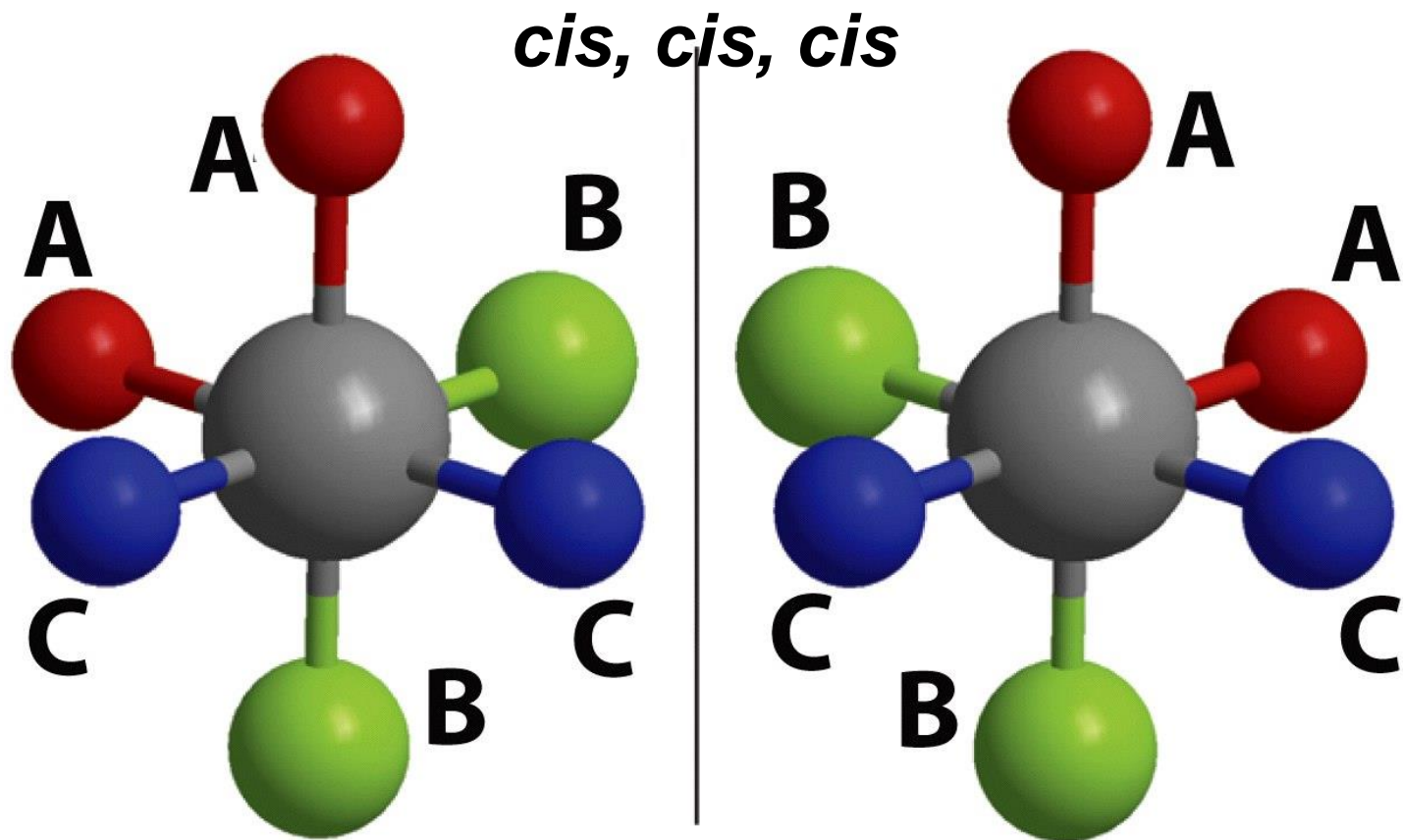
*cis, trans, cis*





*cis, cis, trans*



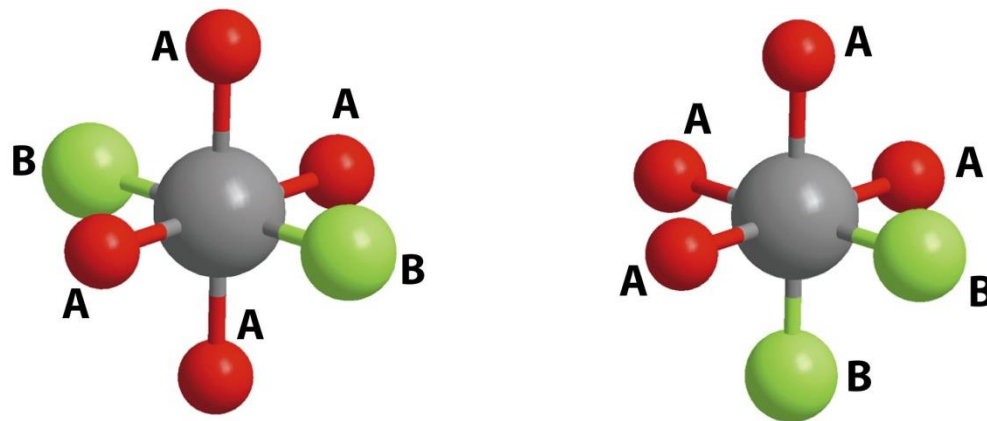


## **[MA<sub>2</sub>B<sub>2</sub>C<sub>2</sub>] enantiomers**

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.*



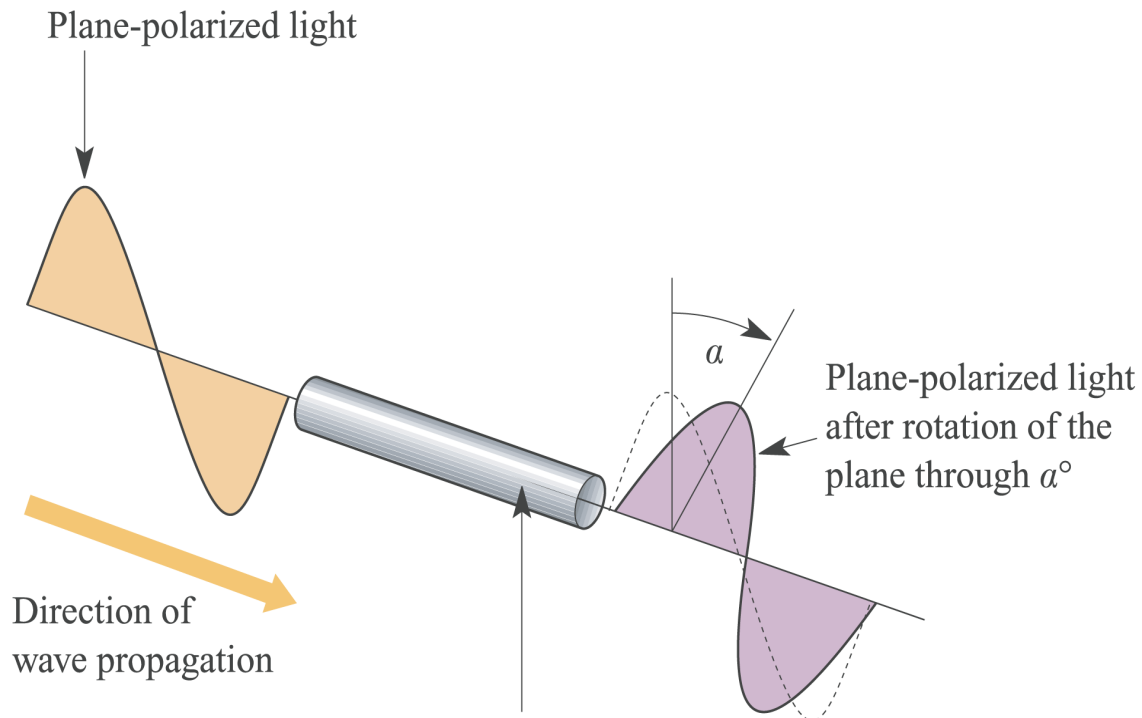
M = centro stereogenico non-chirale

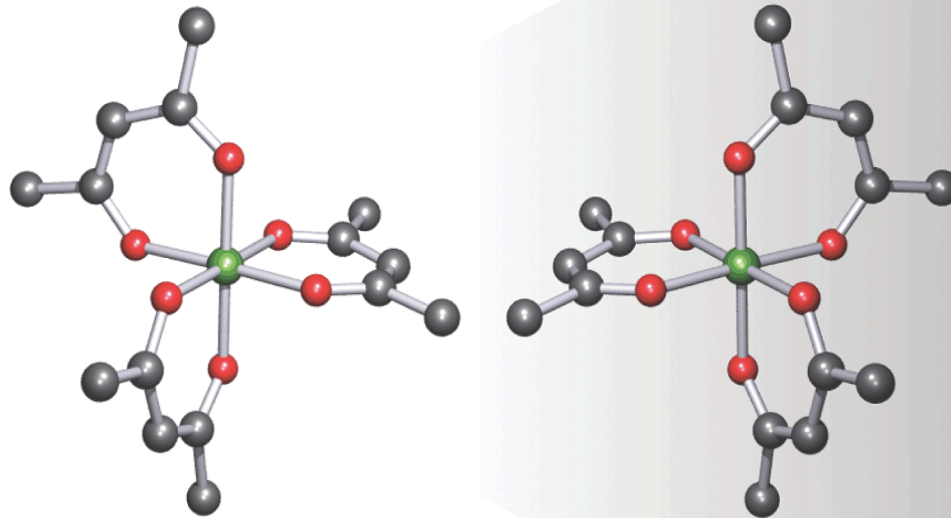


# Enantiomeri

- *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*

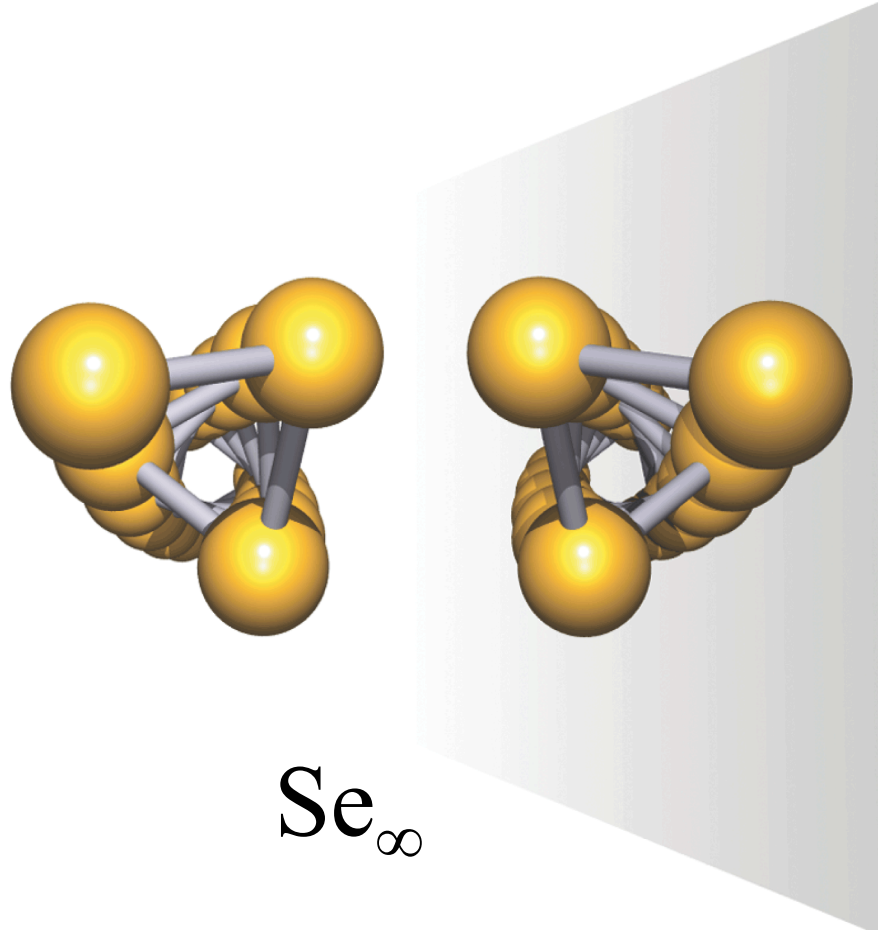




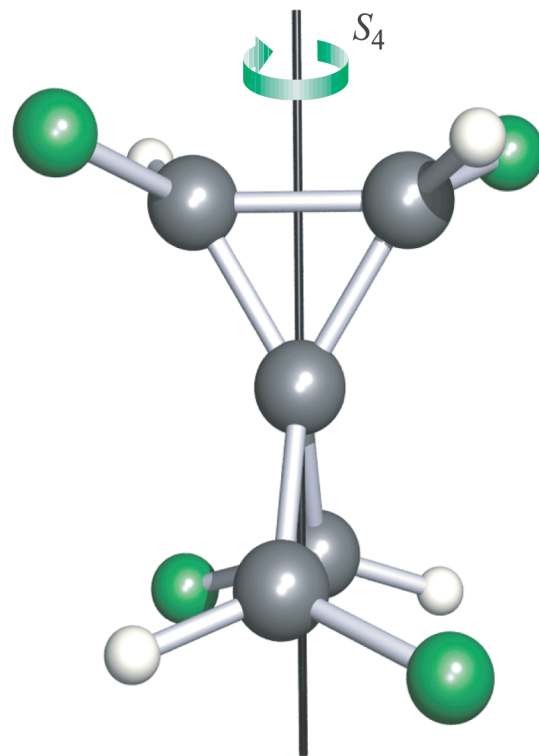
$\Delta$ -enantiomer

$\Lambda$ -enantiomer

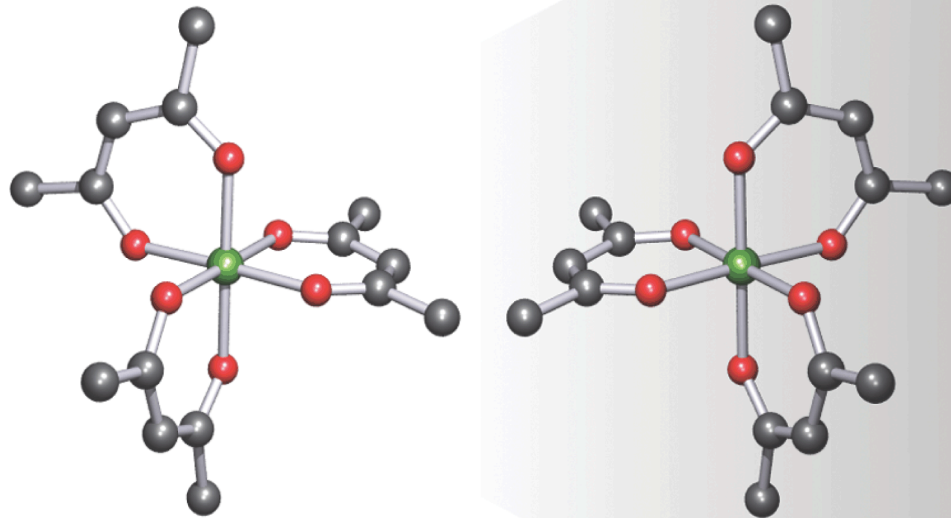
*ogni molecola che non abbia  $S_n$  è chirale*



$\text{Se}_8$



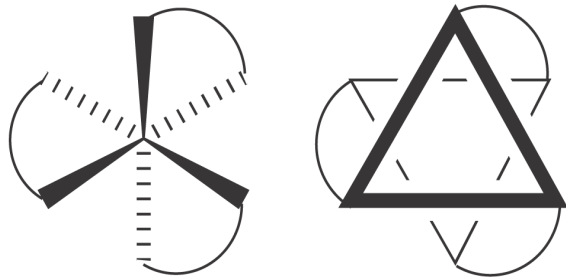
Tetrafluoro-spiropentano,  $S_4$ , achirale



$\Delta$ -enantiomer

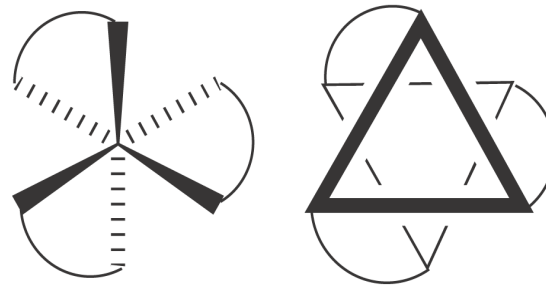
$\Lambda$ -enantiomer

elica destrorsa

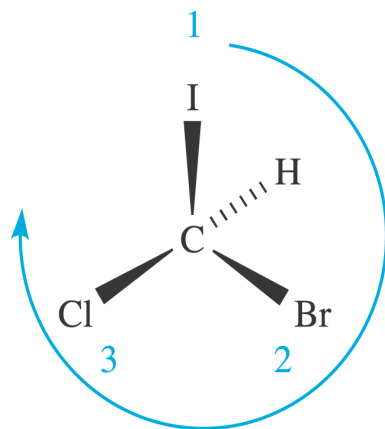


$\Delta$

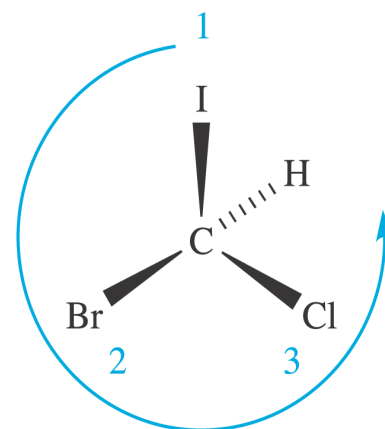
elica sinistrorsa



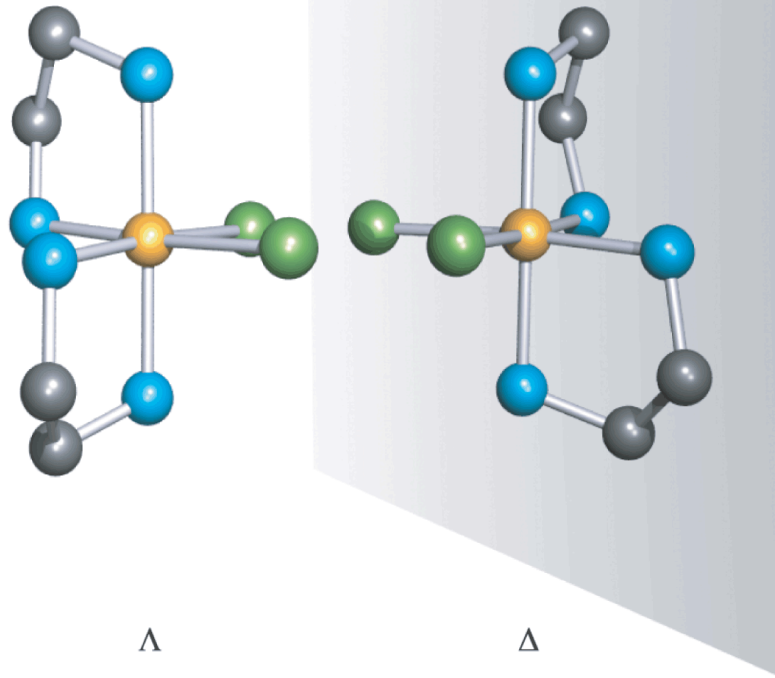
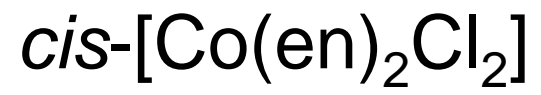
$\Lambda$



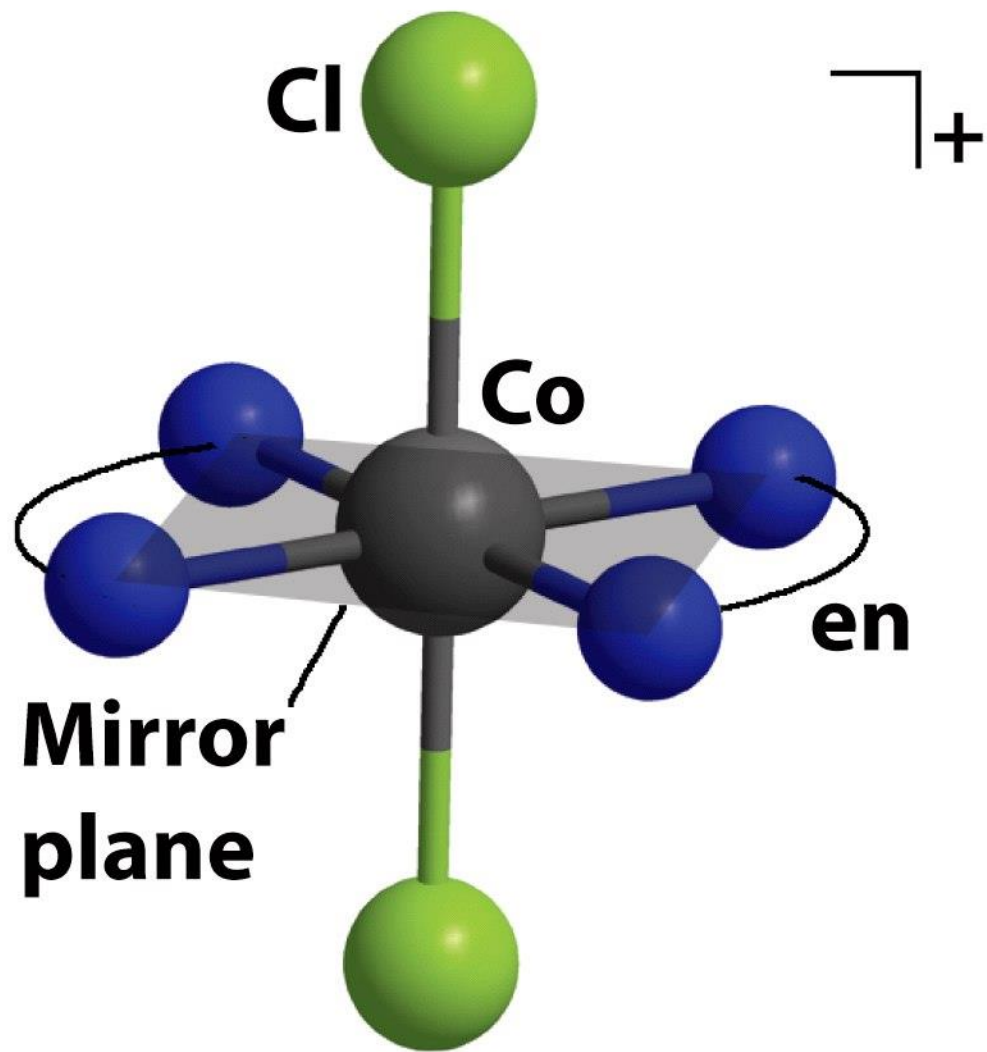
*R*

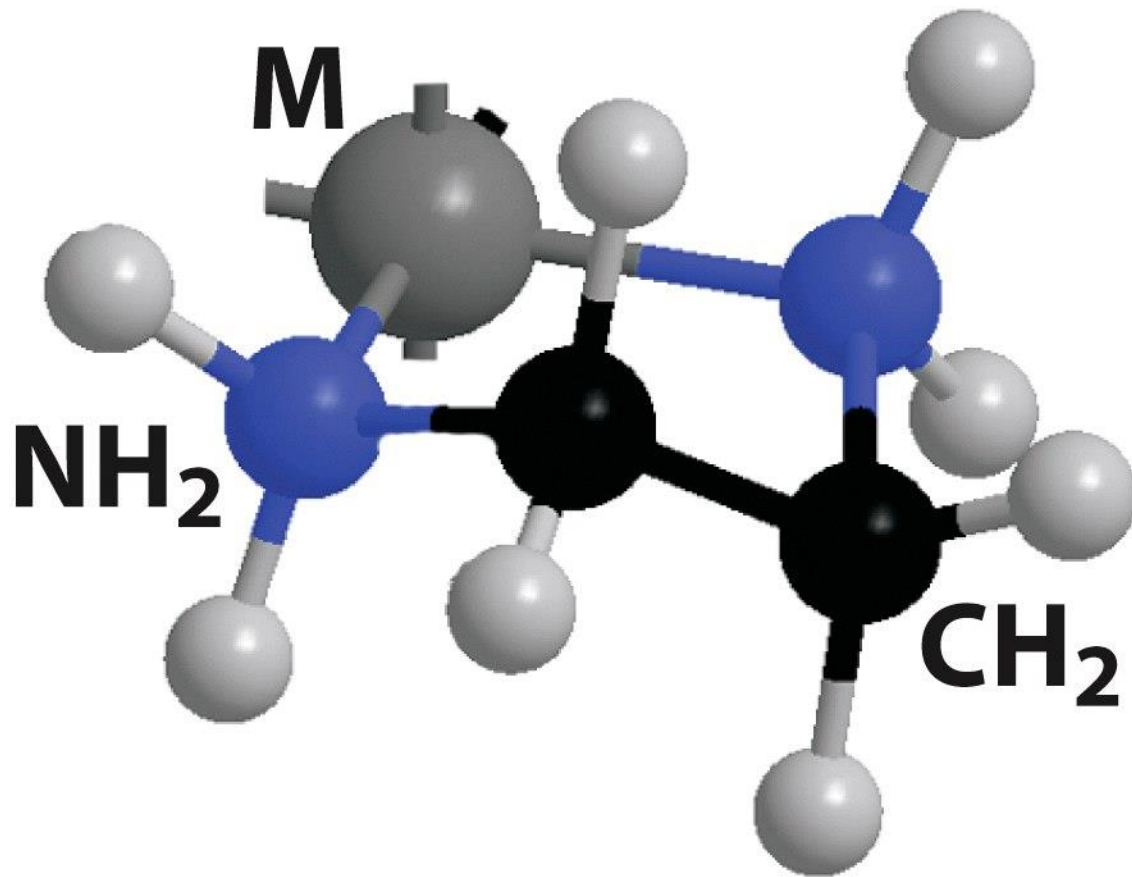


*S*

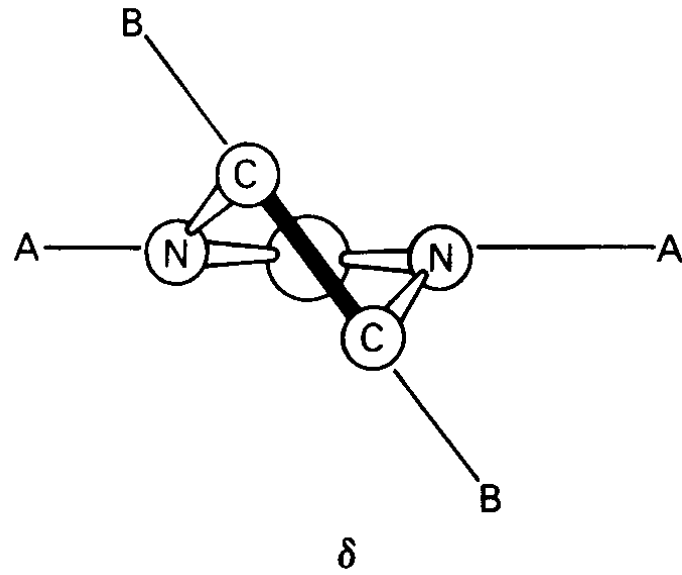
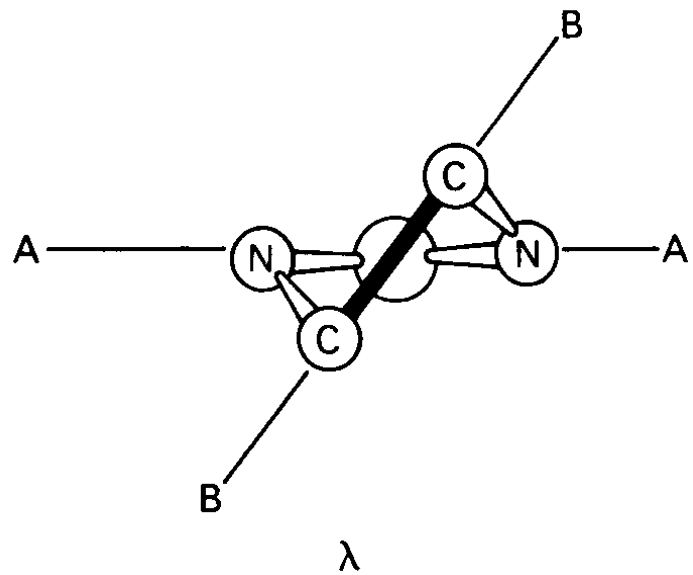


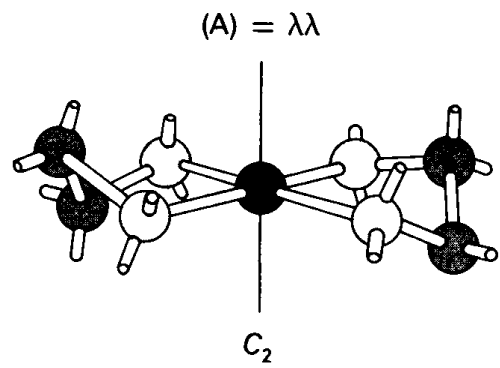
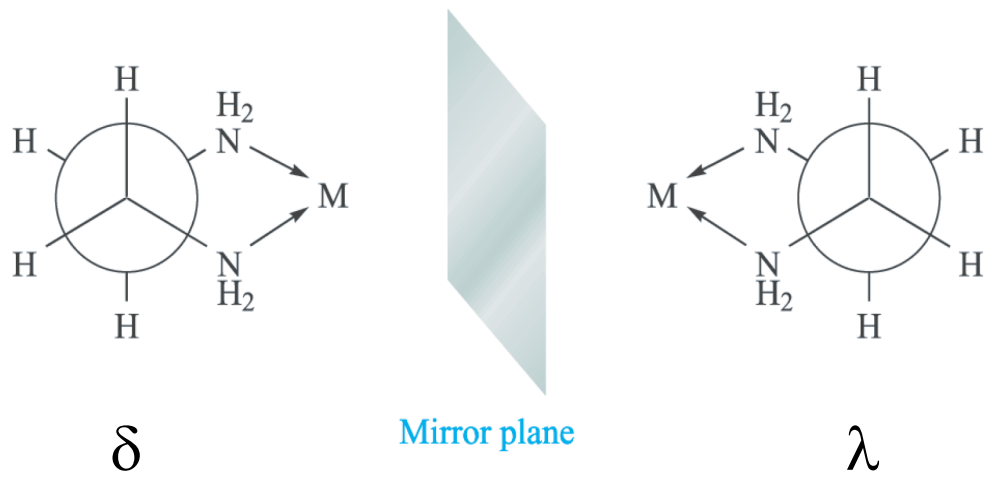




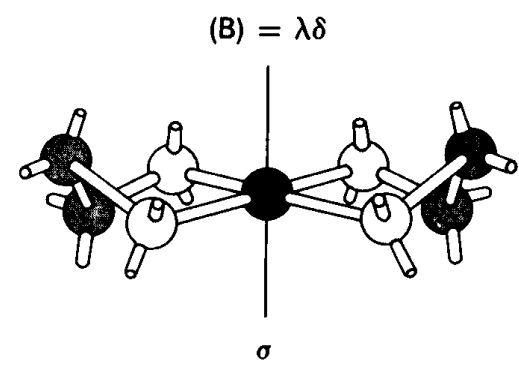


**Ethylenediamine (en)  
ligand attached to M**

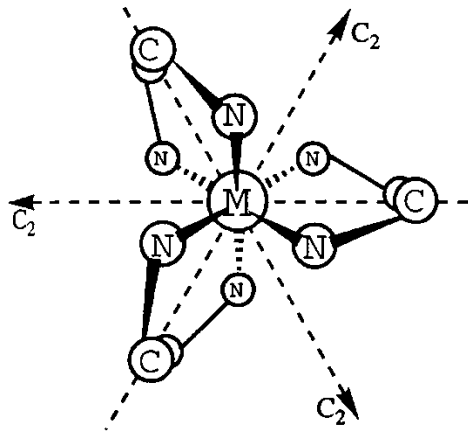




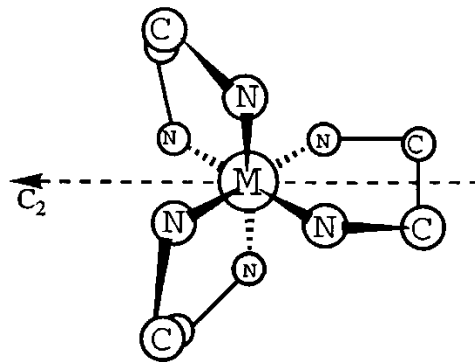
*Rings related by  $C_2$  axis  
H's on adjacent N's are staggered*



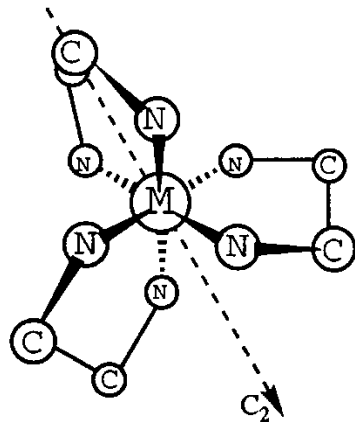
*Rings related by mirror plane  
H's on adjacent N's are eclipsed*



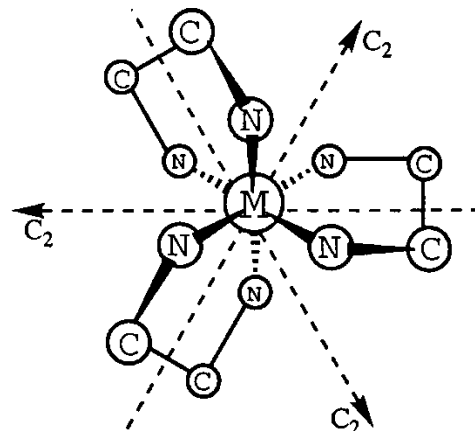
(a)  $\Lambda(\delta, \delta, \delta)$   
 $D_3$



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



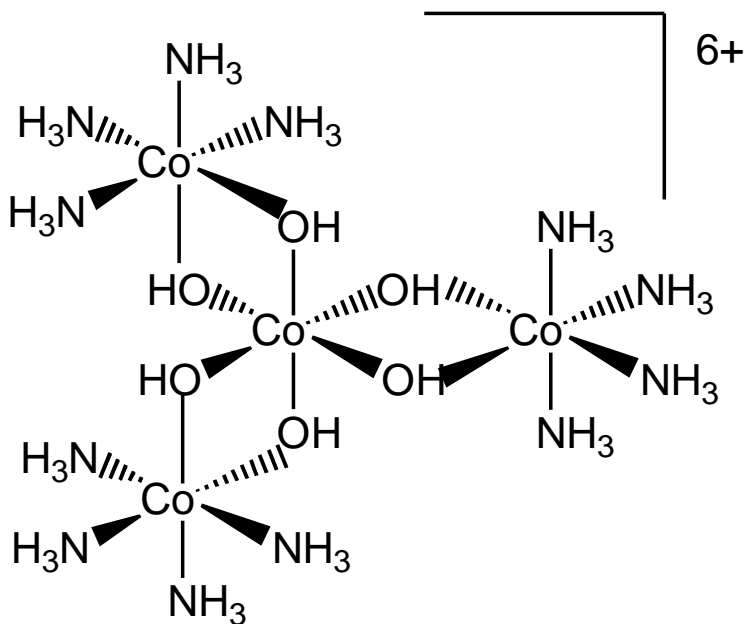
(c)  $\Lambda(\delta, \lambda, \lambda)$   
 $C_2$



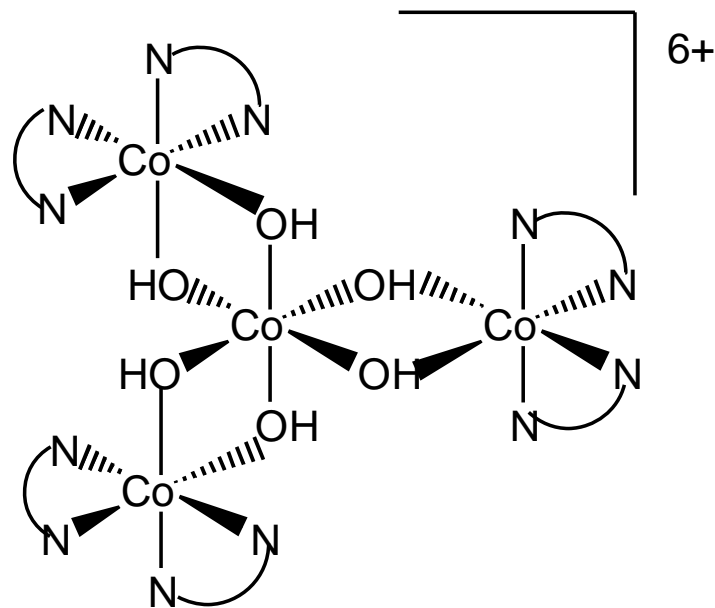
(d)  $\Lambda(\lambda, \lambda, \lambda)$   
 $D_3$

208 ( $\lambda e \delta$ )

2912 ( $R e S$ )



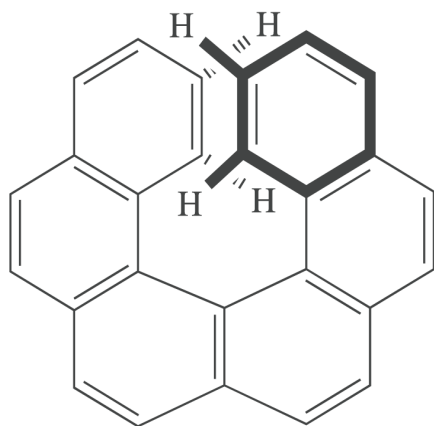
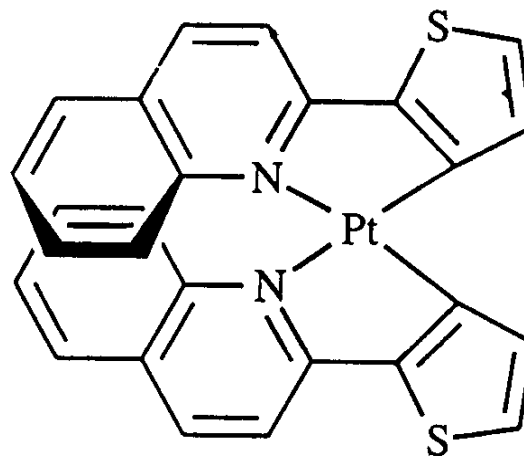
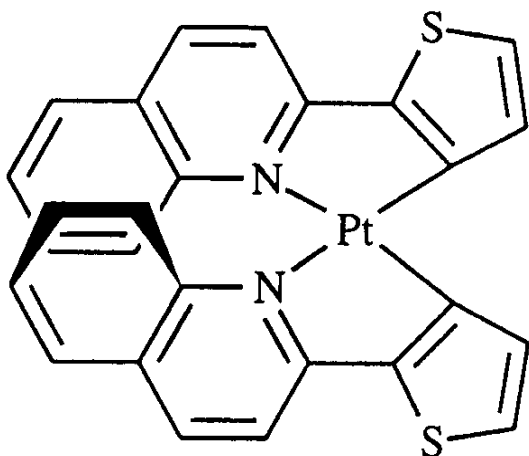
$\Lambda e \Delta$



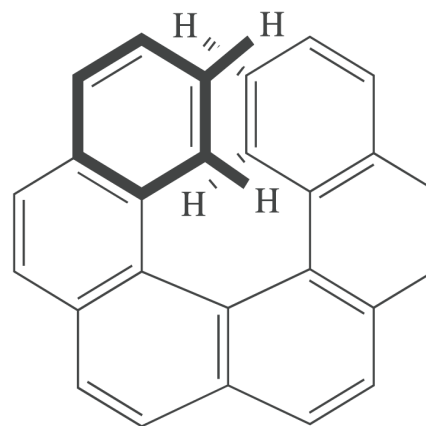
$\Delta(\Delta)_3$	$\Lambda(\Lambda)_3$
$\Delta\{(\Delta)_2\Lambda\}$	$\Lambda\{(\Lambda)_2\Delta\}$
$\Delta\{\Delta(\Lambda)_2\}$	$\Lambda\{\Lambda(\Delta)_2\}$
$\Delta(\Lambda)_3$	$\Lambda(\Delta)_3$

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

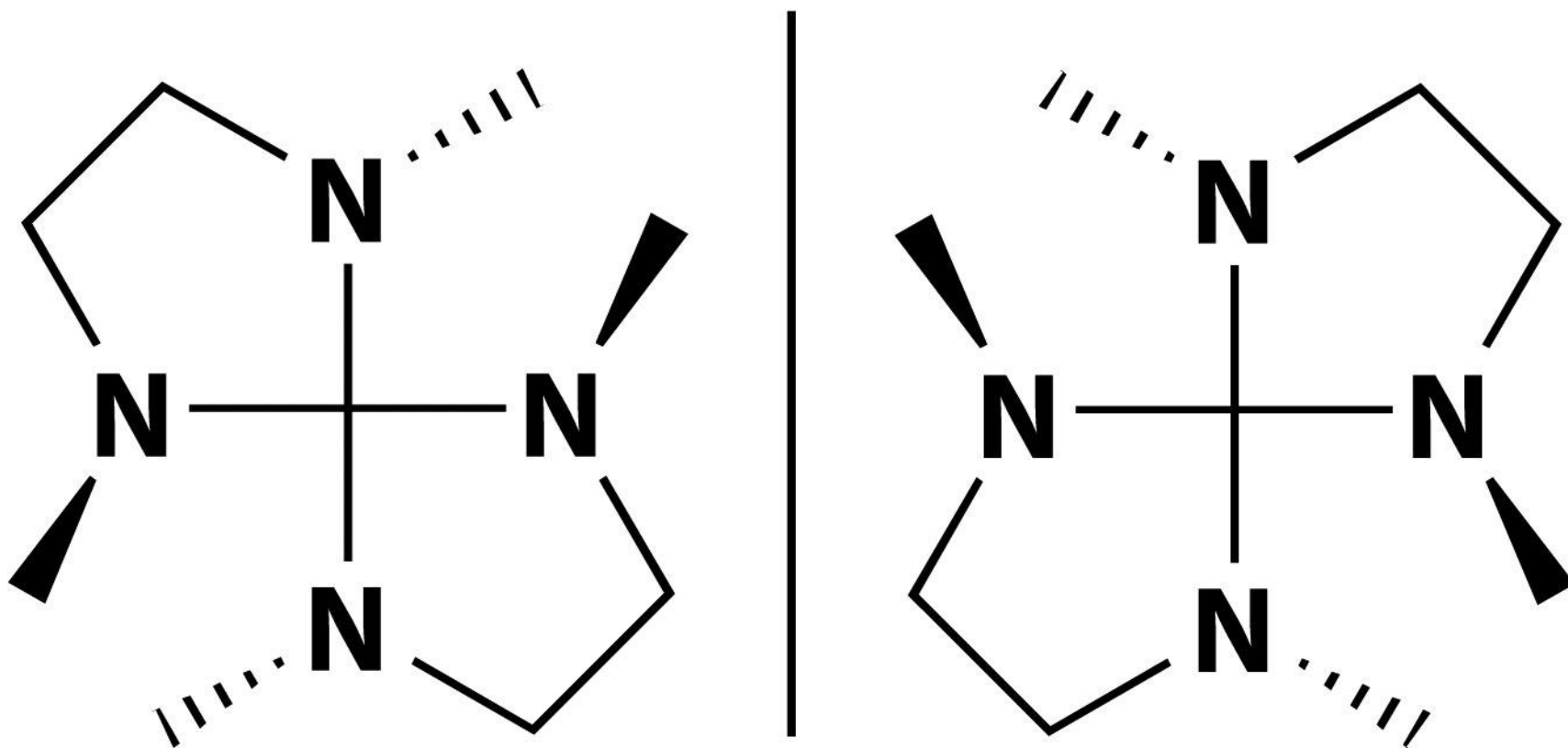
# Chiralità nei complessi planari quadrati



*(P)*-hexahelicene



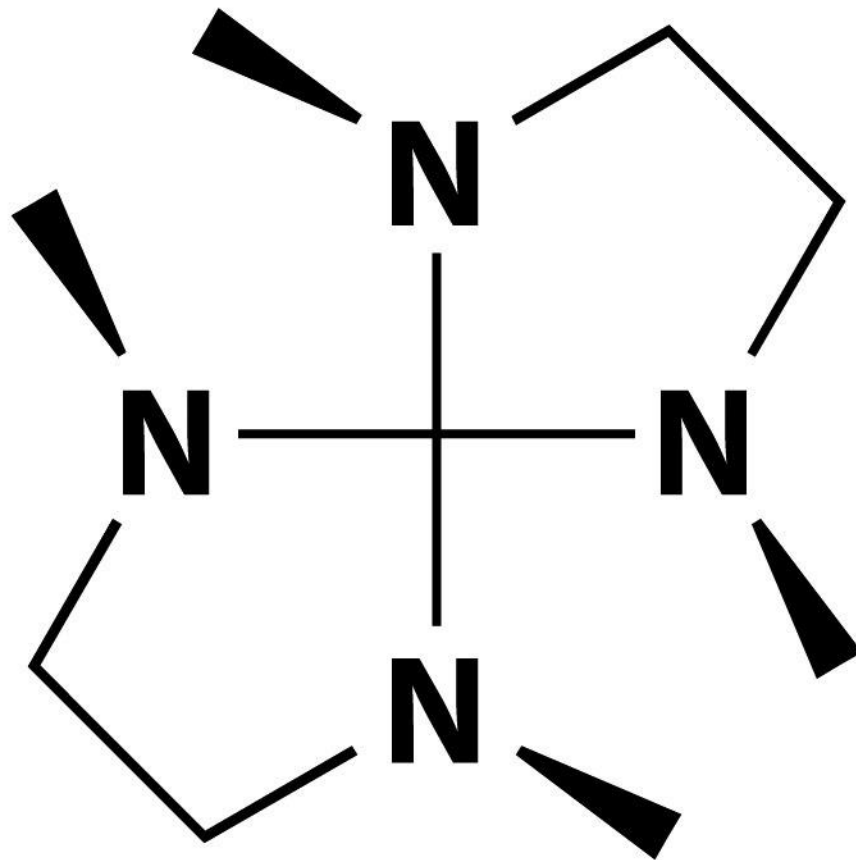
*(M)*-hexahelicene



*racemo*

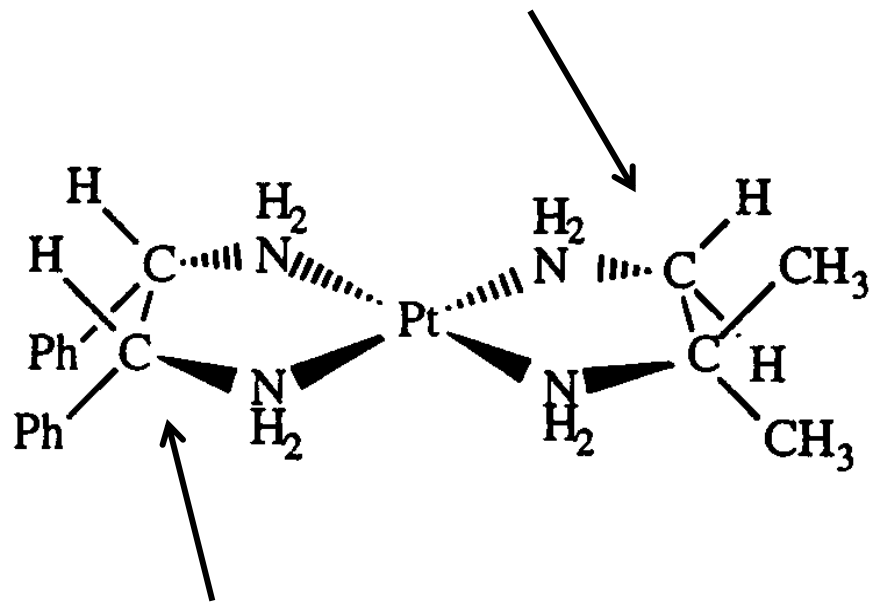
N diventa chirale in seguito alla coordinazione





*meso*

isobutylene-diammina



*meso*-stilbenediammina

