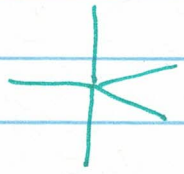
## Lecture VIII: Chirality in Other Molecular Shapes

01-31-202

While tetrahedral chirality finds itself very common in organic chemistry, other molecular shapes can be chiral too. Because of the larger number of substituents, those geometries are often more complex. Exercise: how many isomers can there for $CA_4$, $CA_3B$, $CA_2B_2$, $CA_2BC$, $CABCD$?

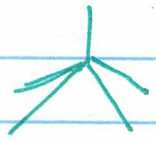
### Coordination Number 5

trigonal bipyramid



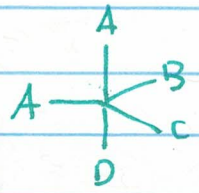
or

square pyramid

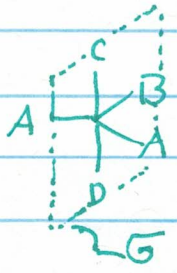


↳ In the $MA_5$ case, this is highly symmetric – four planes of symmetry. Do all five ligands need to be different for this to become chiral?

NO – only four need to differ:

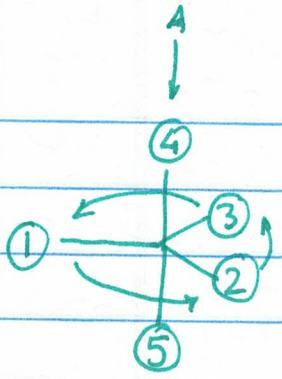



is chiral, but




is not!

How do we name this? Because there are more than two equivalents for a given set of ligands, R and S is no longer sufficient. Two sets of designators are needed:




Looking down the axial axis, from the side of the higher priority ligand:

equatorial ligands are connected clockwise: C

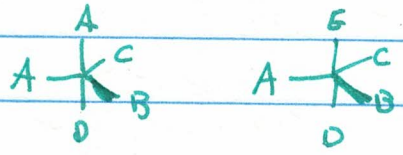
" " " " counterclockwise: A

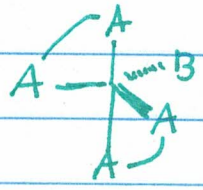
A/C are used to avoid confusion with R/S, which are used only for tetrahedral compounds. They are chirality symbols.

Configuration index is the 2nd parameter needed, and it applies to achiral isomers too. It is a two digit number which gives the ranking of the two axial groups:

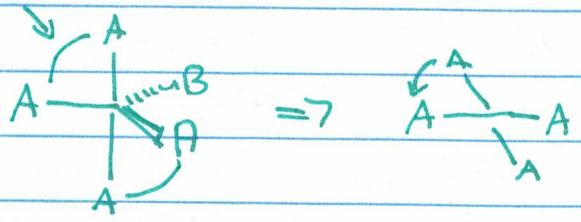
In the case above: 45-A.

Chiral situations, in principle:



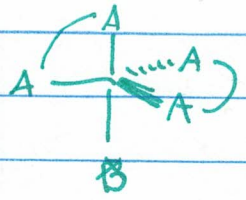




this is now chiral even with symmetric A⌒A chelating ligands what is the Λ or Δ configuration?




now we turn A in the back to coincide with the front around the acute angle: Λ

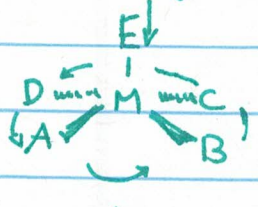
But again, this compound can have an achiral isomer:




However, all of these complexes are dynamic! They go to the square pyramid arrangement and equilibrate with their enantiomer!

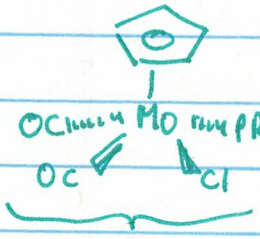
Isolation of chiral pure enantiomers is more likely in the square

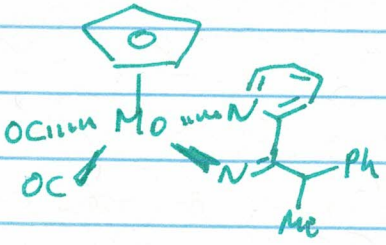
pyramidal geometry:

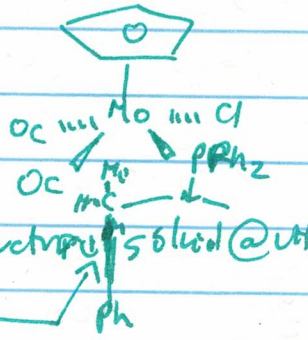



Configuration index: priority ranking of the apex ligand (5 here), followed by the priority ranking of the ligand trans to the highest priority ligand (3 here): 53-A

Cp complexes fall into this category: Chem. Comm. 1978, 691




again, only for ligands need to be different

Structure solved @

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Coordination number 6: octahedral and trigonal pyramid, but octahedral complexes dominate. What tetrahedral geometry is for carbon, octahedral is for metals. But things are much more complicated now.

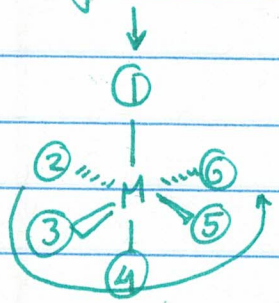
Looking just @ complexes with monodentate ligands:

$MA_6$
$MA_5B$
$MA_4B_2$
$MA_3B_3$
$MA_4BC$
$MA_3B_2C$
$MA_2B_2C_2$
$MA_3BCD$
$MA_2B_2CD$
$MA_2BCDE$
$MABCDEF$

a total of 75 isomers when all stereoisomers are counted!

↳ even one example of this was isolated!

MABCDEF case has 30 isomers – 15 pairs of enantiomers. Assignment of a designator is:



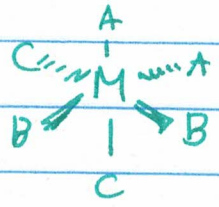

Configurational index:
~~Start~~ ranking of this ligand trans- to highest
+ " " " " " " "
in a plane perpendicular to viewing axis

(A)-chirality symbol, counterclockwise rotation

45 :-
two case.

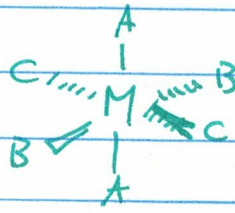
$MA_2B_2C_2$:

here, we can use configurational indices,
or cis/trans relationships.



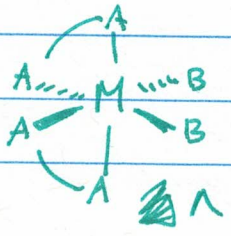

cis, cis, cis – CHIRAL
32-C

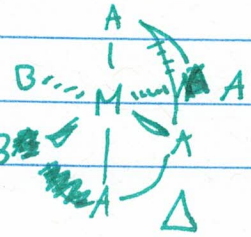
three cis/cis/trans combinations – all achiral

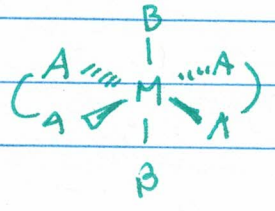



trans, trans, trans – ACHIRAL
12

What happens with bidentate ligands:

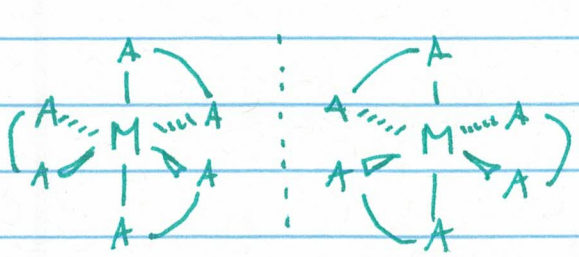


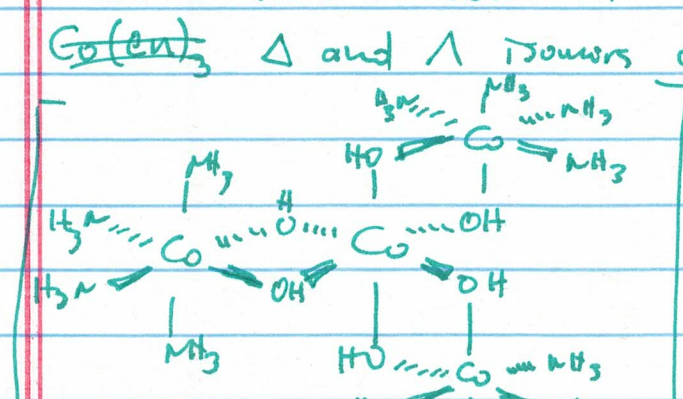

ACHIRAL

Classical case is $M(AA)_3$:



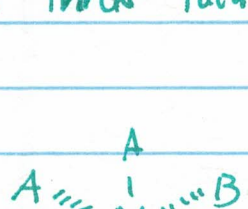
→ but in the case of different bidentate ligand, Δ,Δ,Δ or Λ,Λ,Λ model to applied

Stereoisomerism in coordination compounds was discovered using ~~Co(en)$_3$~~ Δ and Λ isomers of a complex known as luteol:

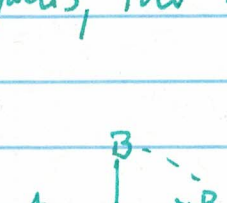


Isolated by Werner in 1907.
Ber. Dtsch. Chem. Ges. 1907, 40, 2103

With three identical ligands, two new isomer classes are found:



$B_3M$ unit is coplanar
mer (meridian)



$B_3M$ unit not coplanar
fac (facial)

both are achiral, but exchanging A for 3 different ligands can make them ch