Lecture XXIV: Conformations of $Co(en)_3^{3+}$

03-30-2020

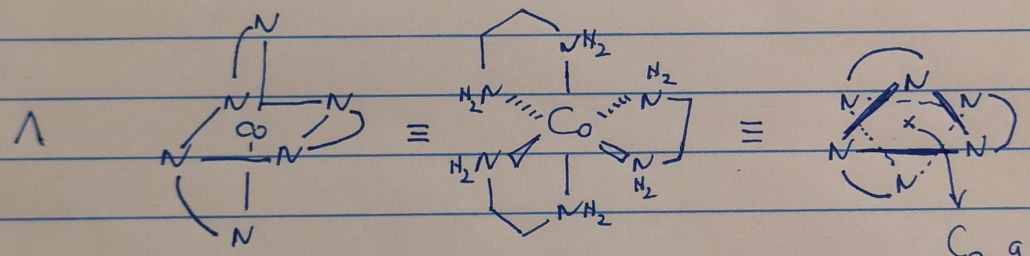
Today's class is entirely based on an excellent tutorial review by John Gladysz from Texas A&M University:

Chem Soc Rev, 2016, 45, 6799

Werner reported that $Co(en)_3^{3+}$ is chiral in 1911. Many analogous complexes of other metals were subsequently discovered:

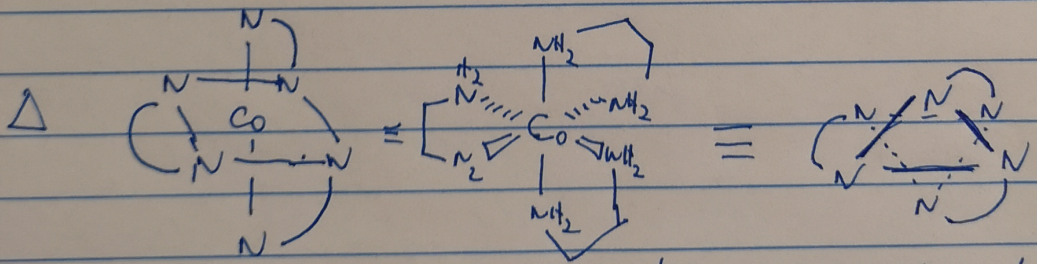
$Cr(en)_3^{3+}$ $Rh(en)_3^{3+}$ $Ir(en)_3^{3+}$ $Pt(en)_3^{4+}$

Two enantiomers come from the chirality of cobalt atom:



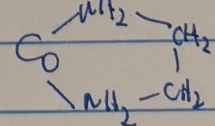
C_3 axis of symmetry

top triangle and bottom triangle connect in a counterclockwise way



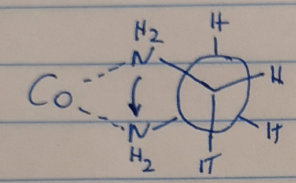
top NNN triangle and bottom one connect in a clockwise fashion

We have seen this before.

But let's dig deeper, focusing on each  chelator

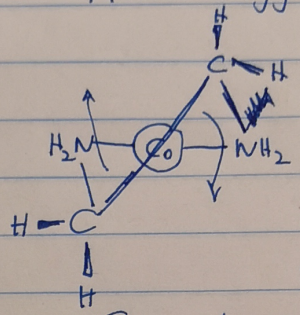
As we have seen last week, these five membered rings are not going to be planar because of eclipsing strain. Instead, ~~the~~ the CH_2CH_2 bridge will distort into a staggered conformation:

Counterclockwise from front to back N

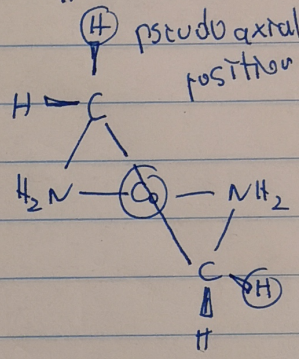


this is λ

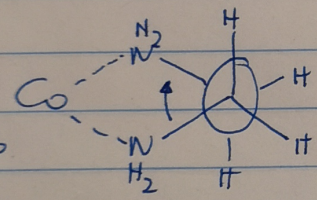
≡



but since two gauche conformations are enantiomeric, we can have the other one too



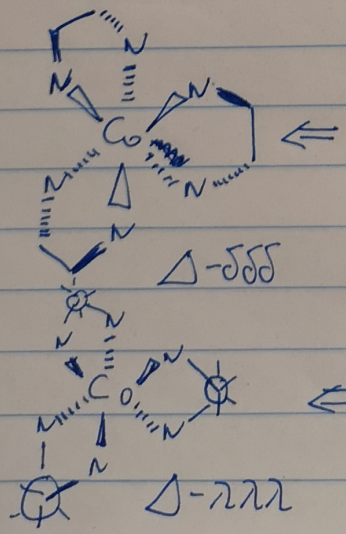
Clockwise from front to back N



this is δ

≡

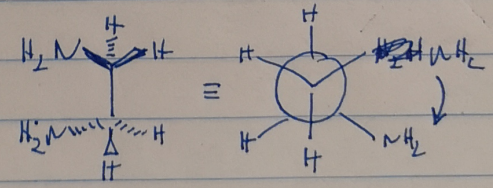
λ and δ are conformers and they equilibrate in solution, but not in the solid state: they are a part of the characterization of the crystal structure. How do three of these come together in $Co(en)_3$?



Δ-$\delta\delta\delta$

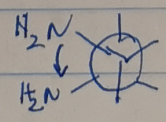
Δ-$\lambda\lambda\lambda$

⇐



≡

δ



λ

$\lambda\lambda\lambda$ is occasionally called lel bc C–C is parallel to C_3 axis

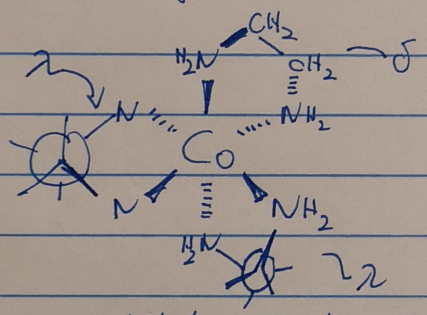
$\delta\delta\delta$ is called ob bc C–C is oblique to C_3

For Λ complexes, this relationship is inverted. There is a total of eight diastereomers:

enantiomers	Λ-λλλ	Λ-δλλ	Λ-λδδ	Λ-δδδ
	ob$_3$ / D$_3$	ob$_2$ lel / C$_2$	ob lel$_2$ / C$_2$	lel$_3$ / D$_3$
	⇕	⇕	⇕	⇕
	Δ-δδδ	Δ-λδδ	Δ-δλλ	Δ-λλλ
	ob$_3$ / D$_3$	ob$_2$ lel / C$_2$	ob lel$_2$ / C$_2$	lel$_3$ / D$_3$

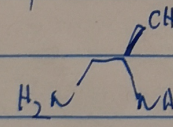
the stabilities of all of these are within 2 kcal/mol

Practice drawing these! For Δ-λδδ, as an example:



Monosubstituted ethylenediamine ligands

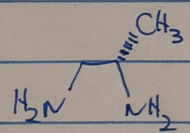
If H_2N–NH_2 is replaced with H_2N–CH(CH$_3$)–NH_2, the complexity additionally increases:



(R)-1,2-propylenediamine

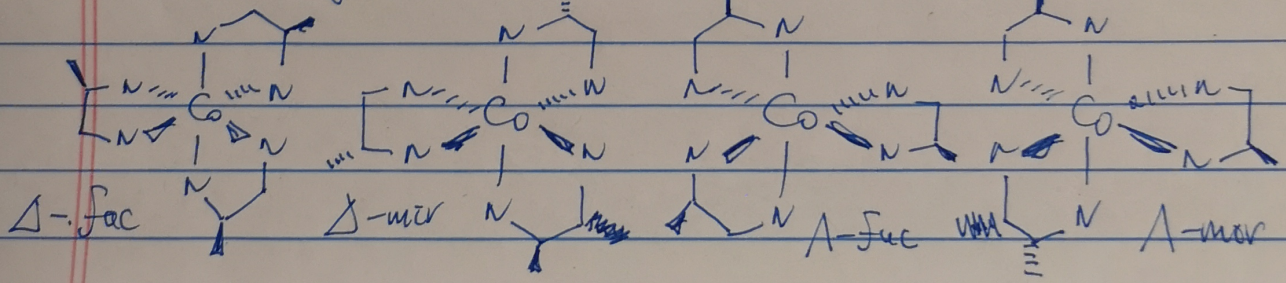
(R)-pn

or



(S)-pn

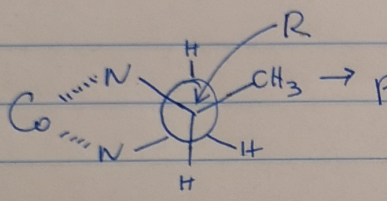
In taking homochiral, e.g. all-(R), four diastereomers



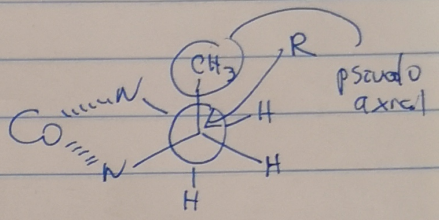
Δ-fac Δ-mer Λ-fac Λ-mer

We have seen fac- and mer- designators before. With (S)-pn, we have four more stereoisomers; and with mixed (S)/(R) combinations, there are even more—and all are chiral!

Each of the $Co(pn)_3^{3+}$ isomers also has conformers



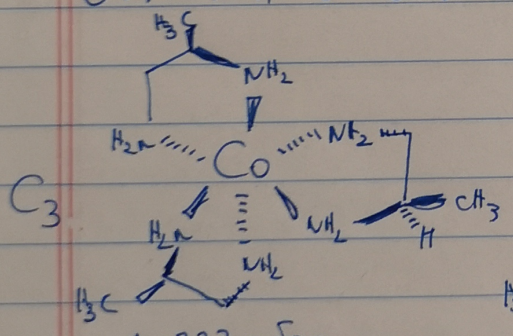
→ pseudoequatorial



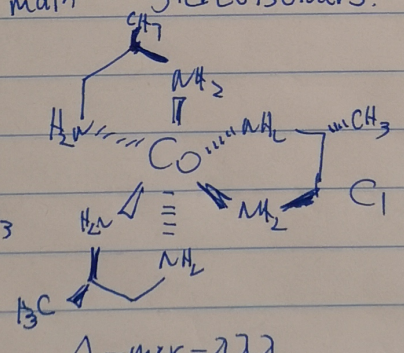
λ-is now more stable; in $Co(en)_3^{3+}$ they were more similar

δ-is now less stable

For (R)-pn, δ-λλλ (Δ-fac_3) and Λ-λλλ (Λ-do_3) are now favored. For (S)-pn, these switch, so Δ-δδδ and Λ-δδδ dominate. Bringing this together with fac- and mer-, the (R)-pn causes the formation of four main stereoisomers:

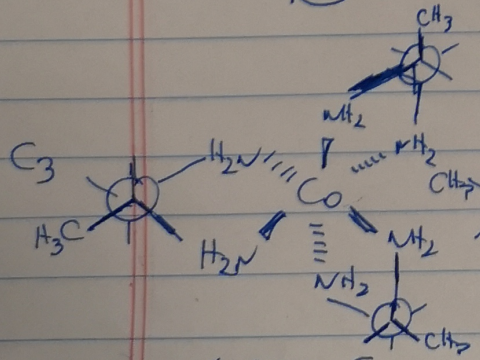


Λ-λλλ-fac

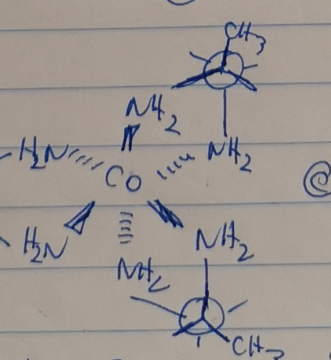


Λ-mer-λλλ

other conformers are less stable

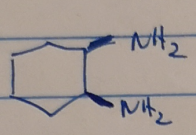


Δ-λλλ-fac

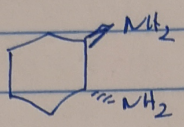


Δ-λλλ-mer

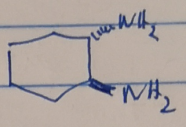
Symmetrically disubstituted en ligands



(R,S)-chxn

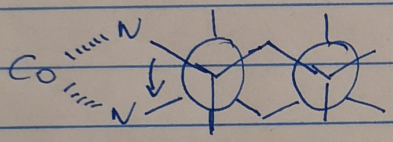


(R,R)-chxn



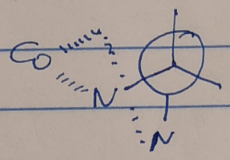
(S,S)-chxn

Let's look at the homochiral case again first: all R,R:



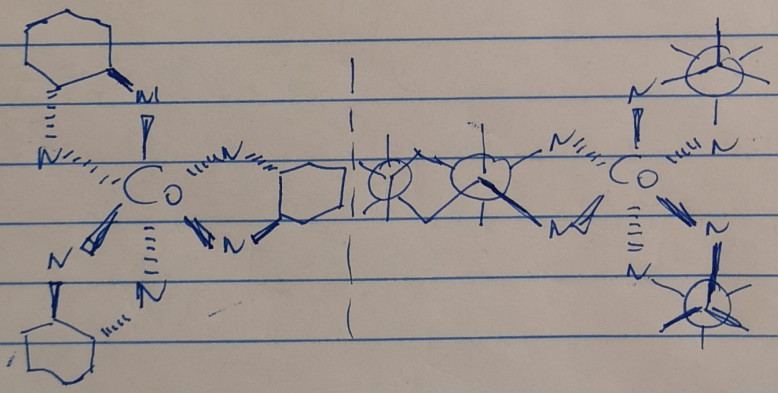
λ-(R,R)

vs



δ-(R,R) → impossible

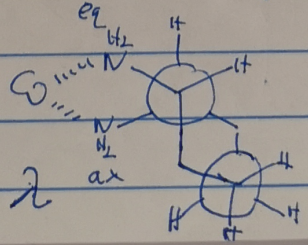
Because the ligand is symmetric, there are no fac- or mer-isomers either



Λ-λλλ ob_3/D_3 Δ-λλλ lel_3/D_3

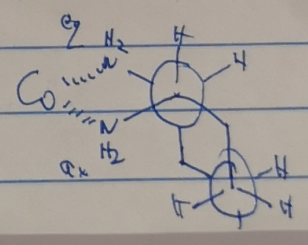
For (S,S)-ligand, λ conformation is impossible, so the options are only Δ-δδδ and Λ-δδδ. If both RR+SS are used → diastereomers!

If we use the meso (R,S) ligand, one NH_2 group is axial, the other equatorial:



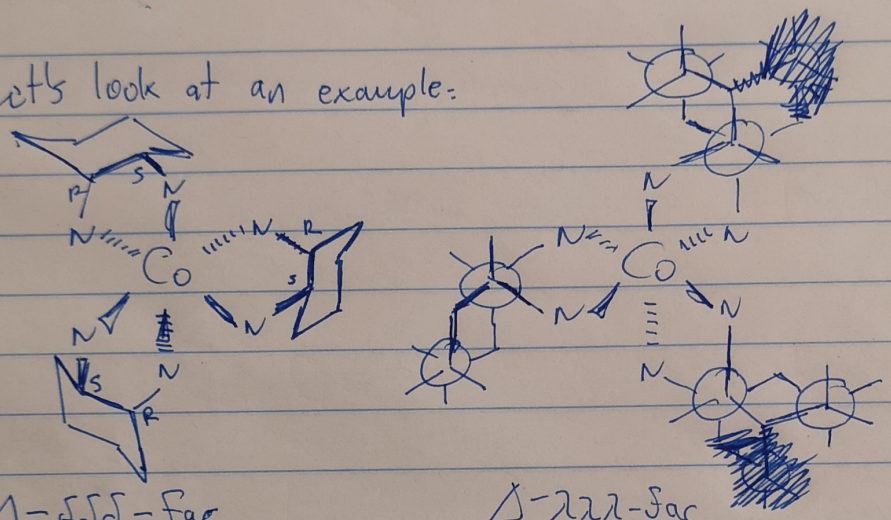
λ

or



$[Co(cis\text{-}chxn)_3]^{3+}$ now again has fac and mer-isomers, and there is a total of 24 stereoisomers: Δ-fac / Λ-fac (4 stereoisomers each)
Δ-mer / Λ-mer (8 " ")

Let's look at an example:



Λ-δδδ-fac
λλλ

Δ-λλλ-fac
plus the Λ-fac-δδδ and Δ-fac-δδδ

This simple system has an incredibly rich stereochemistry! Some of it is now being used in catalysis as well.

PRACTICE DRAWING THESE ISOMERS!