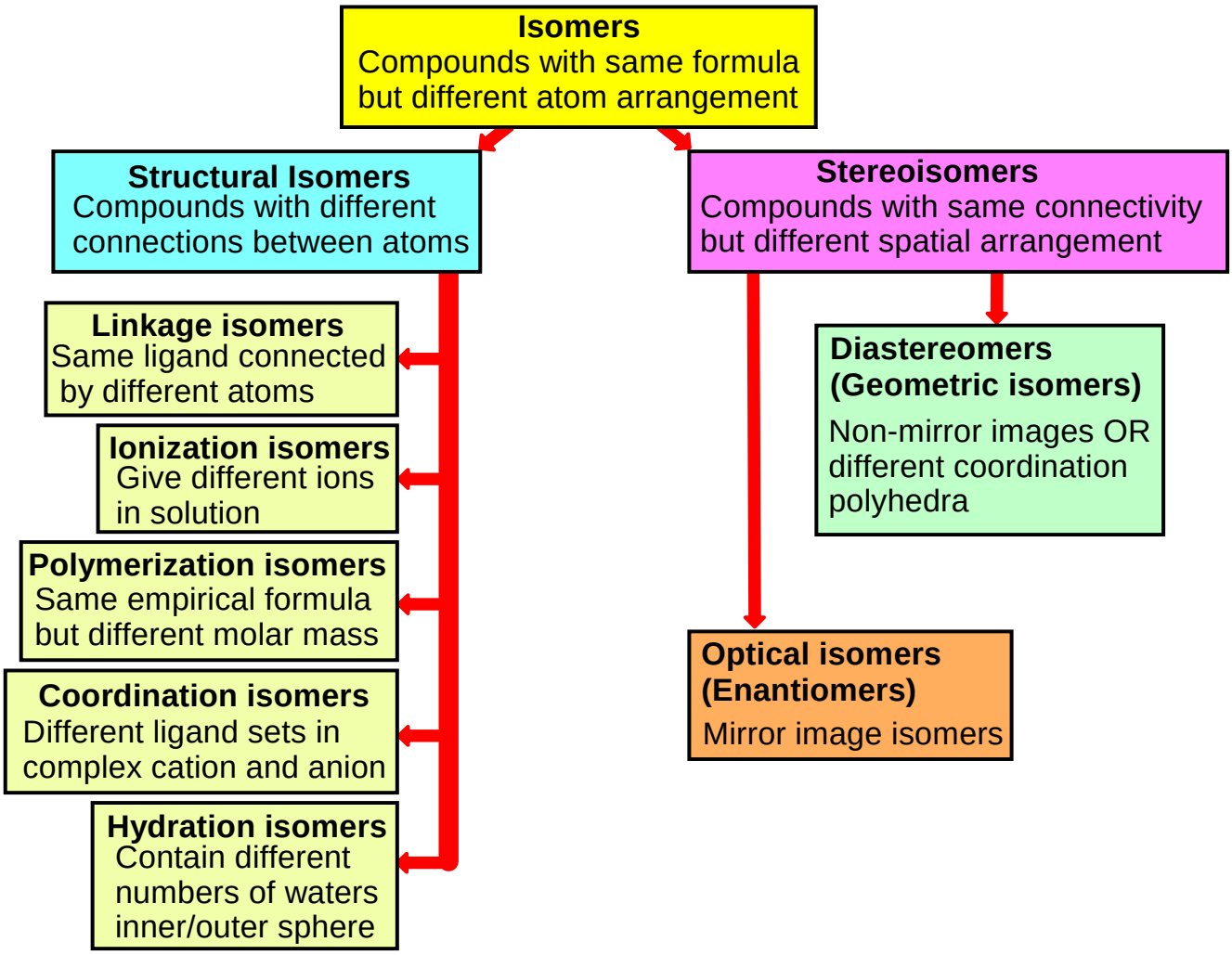
Isomerism in Coordination Chemistry

(Chapter 20 H&S)



Structural Isomerism

Linkage isomers: same ligand connected by different atoms

Ionization isomers: different ions when dissolved

exchange of ions between inner and outer coordination sphere

eg. **$[Co(NH_3)_5Br][SO_4]$** **vs.** **$[Co(NH_3)_5(SO_4)]Br$**

Methods to distinguish these?

Polymerization isomers: identical empirical formulae but different molar masses (i.e. different degrees of aggregation)

Coordination isomers: found in special cases where both the cation and anion are complexes

egs. $[Co(NH_3)_6][Cr(CN)_6]$ *vs.* $[Cr(NH_3)_6][Co(CN)_6]$

$[Pt(NH_3)_4][PtCl_6]$ *vs.* $[Pt(NH_3)_4Cl_2][PtCl_4]$

Hydration isomers: exchange of water and another ligand between inner and outer coordination sphere

eg. $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (green crystals from c. HCl soln)

→ (dissolve H_2O) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (blue-green)

→ (heat) $[Cr(H_2O)_6]Cl_3$ (violet)

Stereoisomerism

Diastereoisomers (geometrical isomers): essentially includes all isomers that have the same M-L connectivity but a different spatial arrangement of donors AND are not mirror image isomers

Note: this wider definition includes what are often termed 'geometrical' isomers such as cis/trans complex and complexes of different polyhedral arrangements (eg. sq. pyramidal vs. TBP). While strictly correct, some prefer to reserve the term 'diastereomers' for optical isomers that are NOT enantiomers (i.e. in the same way it is used in organic chemistry: eg. RR and RS are diastereomers but not enantiomers)

CN 4

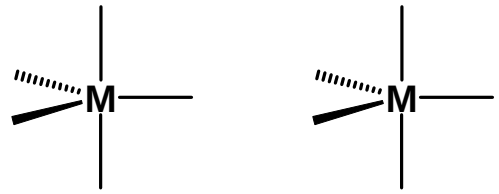
Square planar: ML_2X_2 type

cis and ***trans*** isomers

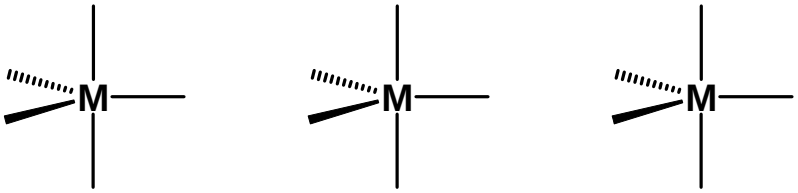
CN 5 (isomers defined below often interconvert)

TBP: MXL_4 and MX_2L_3

MXL_4

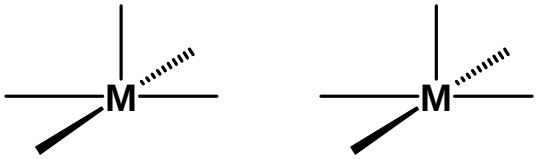


MX_2L_3

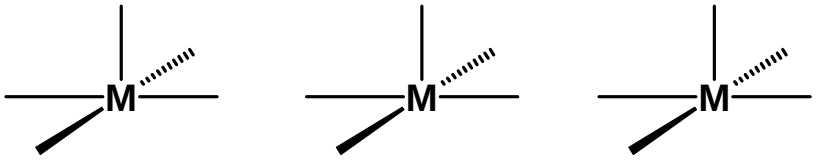


SqPyr: MXL_4 and MX_2L_3

MXL_4

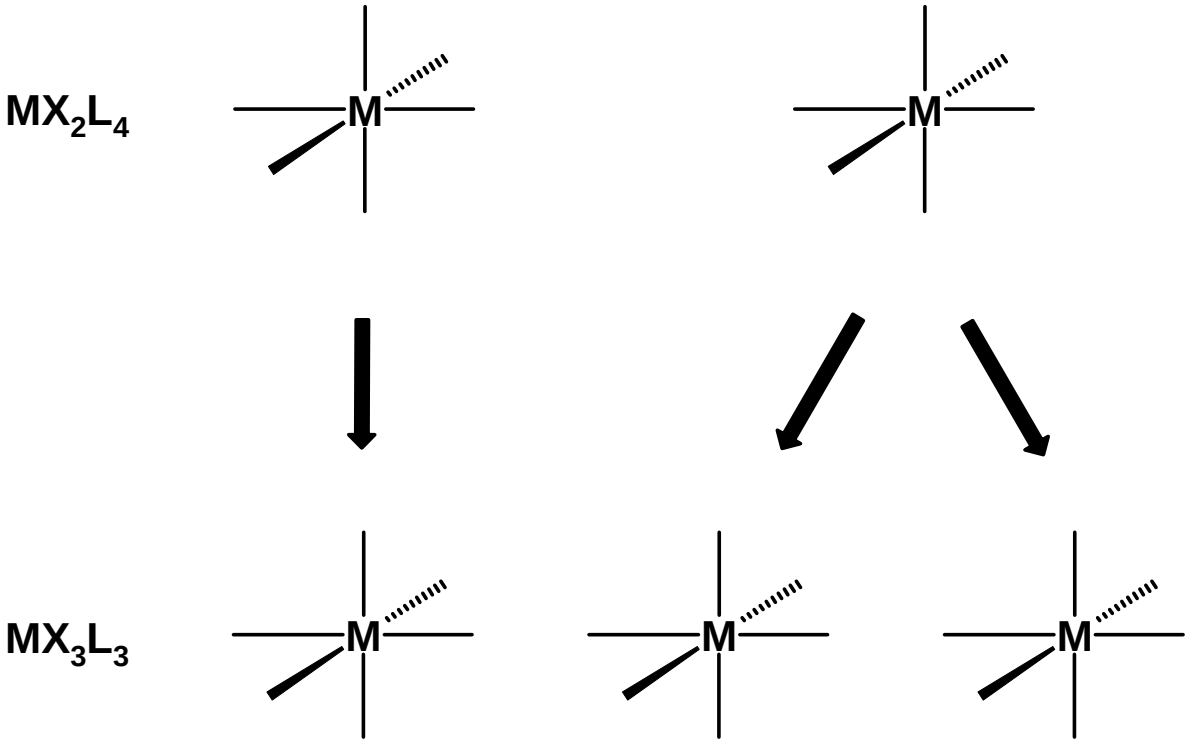


MX_2L_3



CN 6

Oh: all vertices identical so only one structure for MXL_5



Optical isomers (enantiomers): only includes isomers that are optically active (rotate plane-polarized light) and mirror images

Special case in Oh metal complexes:
helical chirality of tris(chelates)

eg. **$Co(acac)_3$**