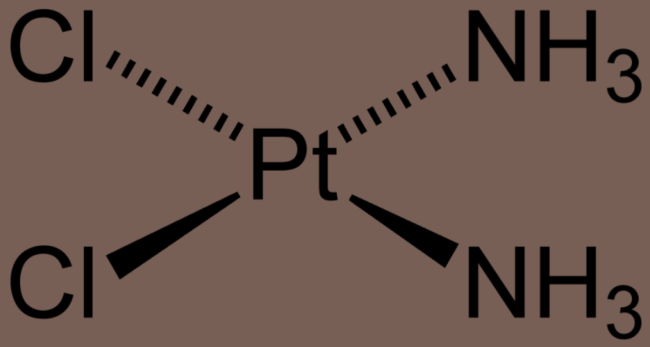
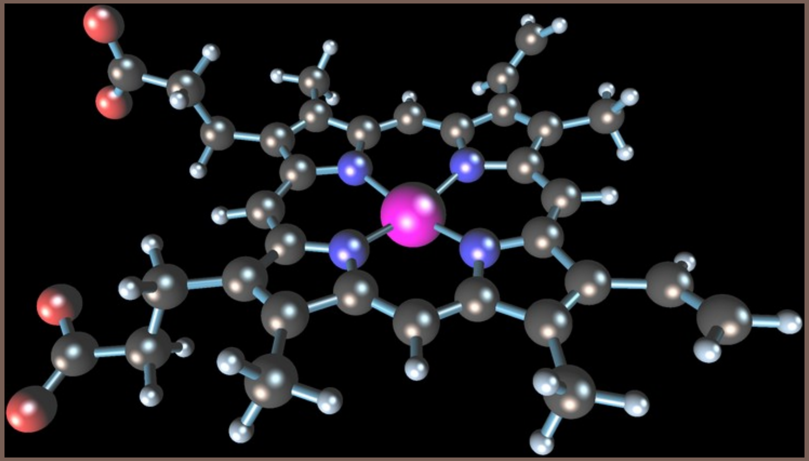
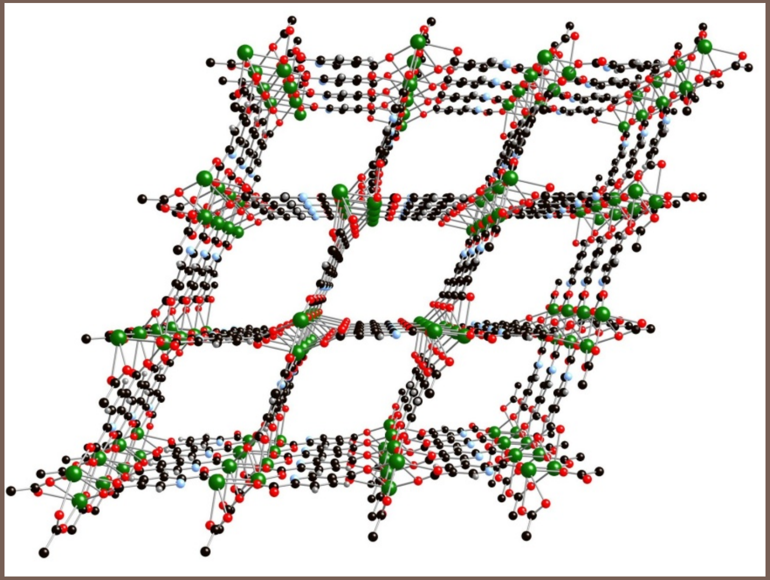
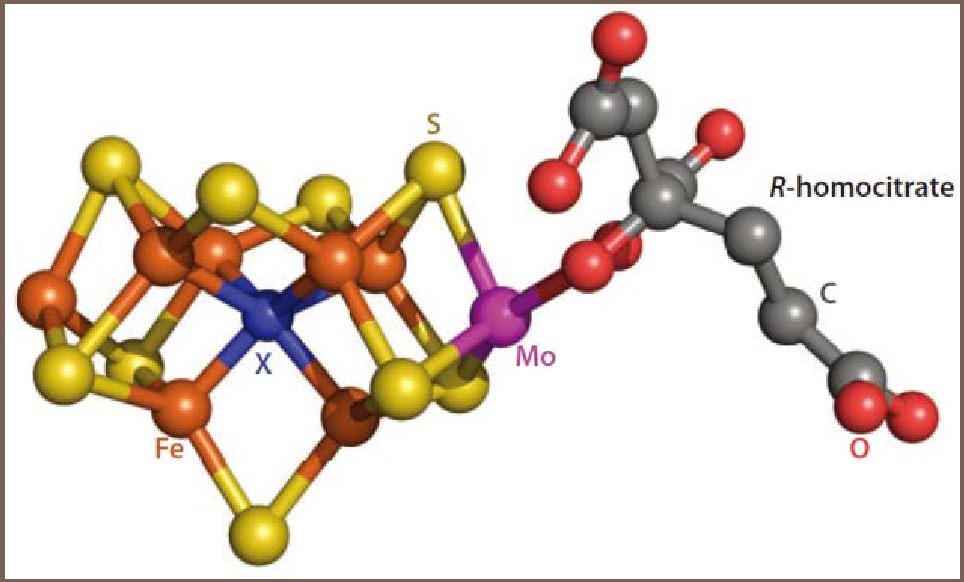




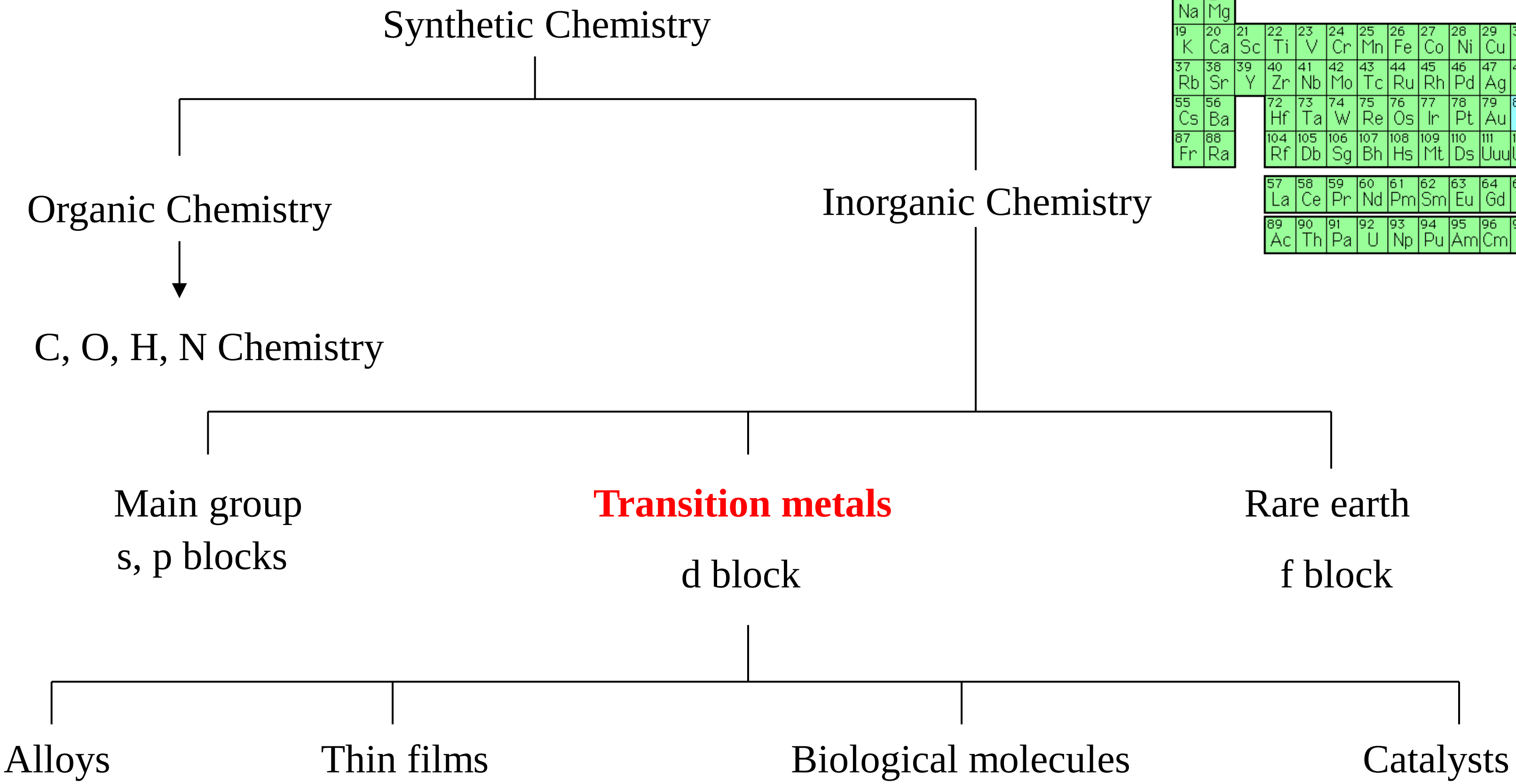




9

Coordination Chemistry I: Structure and Isomers

Synthetic Chemistry



Synthetic Chemistry

Organic Chemistry

C, O, H, N Chemistry

Inorganic Chemistry

Main group
s, p blocks

Transition metals

d block

Rare earth

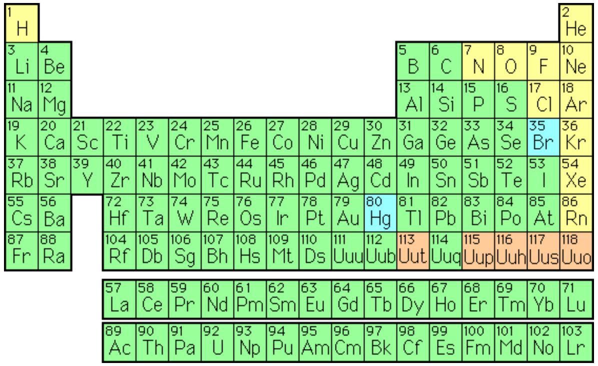
f block

Alloys

Thin films

Biological molecules

Catalysts

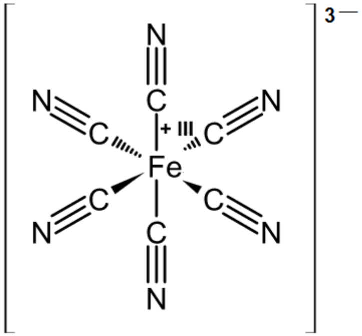


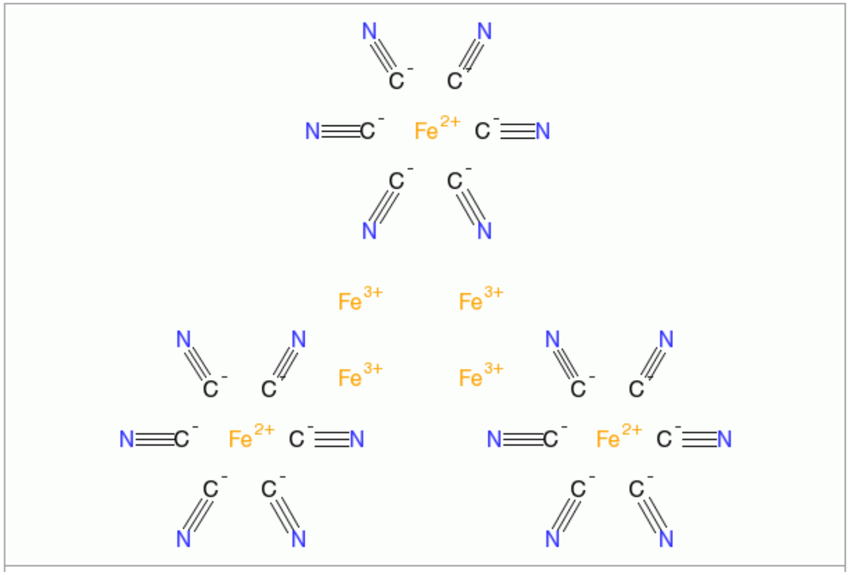
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Uuu	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

History of Coordination Chemistry

Pigments, such as Prussian blue, copper vitriol….

$Fe_7(CN)_{18}$ $CuSO_4$





1798, B. M. Tassaert (France) found that ammonical solutions of cobalt chloride, $CoCl_3$, developed a brownish mahogany color ‘salt’ with composition of $CoN_6H_{18}Cl_3 = CoCl_3(NH_3)_6$.

~ ~ , many Co, Ir, Pt compound were prepared, such as $CoCl_3(NH_3)_6$, $CoCl_3(NH_3)_5$, $CoCl_3(NH_3)_4$, $CoCl_3(NH_3)_3$, $PtCl_4(NH_3)_2$, ……

History of Coordination Chemistry

~ ~ , many Co, Ir, Pt compound were prepared, such as $CoCl_3(NH_3)_6$, $CoCl_3(NH_3)_5$, $CoCl_3(NH_3)_4$, $CoCl_3(NH_3)_3$, $PtCl_4(NH_3)_2$, ……

Empirical formula	Color	Original Name	Equevalence of AgCl precipitate (Blomstrand)	Number of ions predicted from conductivity (Werner)
$CoCl_3(NH_3)_6$	Yellow	Luteocobaltic	3	4
$CoCl_3(NH_3)_5$	Purple	Purpureocobaltic	2	3
$CoCl_3(NH_3)_4$	Green	Praseocobaltic	1	2
$CoCl_3(NH_3)_4$	Violet	Violeocobaltic	1	2
$CoCl_3(NH_3)_3$	Orange		0	0

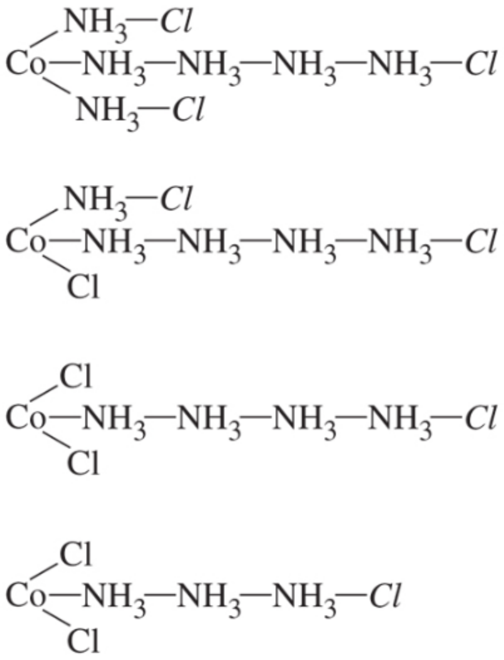
Before Werner, chemists defined the **valence** of an element as the number of its bonds without distinguishing different types of bond.

Ex) Fe: 3, Cl: 1 => $FeCl_3$ Co: 3

History of Coordination Chemistry

1862, Blomstrand suggested

Empirical formula	Equevalence of AgCl precipitate (Blomstrand)	Number of ions predicted from conductivity (Werner)
$CoCl_3(NH_3)_6$	3	4
$CoCl_3(NH_3)_5$	2	3
$CoCl_3(NH_3)_4$	1	2
$CoCl_3(NH_3)_4$	1	2
$CoCl_3(NH_3)_3$	0	0



1892, **Werner** considered that the Co-Cl bonds correspond to a "primary" valence of 3 at long distance, while the Co-NH_3 bonds which correspond to a "secondary" or weaker valence (coordination number) of 6 at shorter distance for $CoCl_3(NH_3)_6$.

$[Co(NH_3)_6]Cl_3$ $[Co(NH_3)_5Cl]Cl_2$ $[Co(NH_3)_4Cl_2]Cl$ $[Co(NH_3)_3Cl_3]$

History of Coordination Chemistry

Empirical formula	Color
$CoCl_3(NH_3)_4$	Green
$CoCl_3(NH_3)_4$	Violet

Werner further proposed octahedral structures of the cobalt complexes. (‘cause it is the only one to have two isomers out of the other possible six-bonded structures)

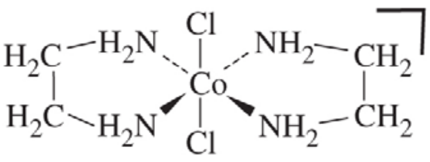
Werner-Jørgensen argument: optical isomer of $[Co(en)_2Cl_2]^+$

Werner: *cis*-$[Co(en)_2Cl_2]^+$

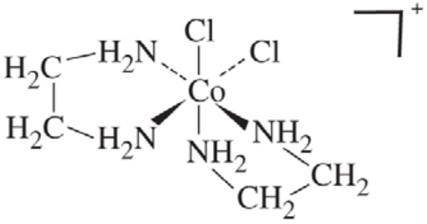
Jørgensen:

coming from C

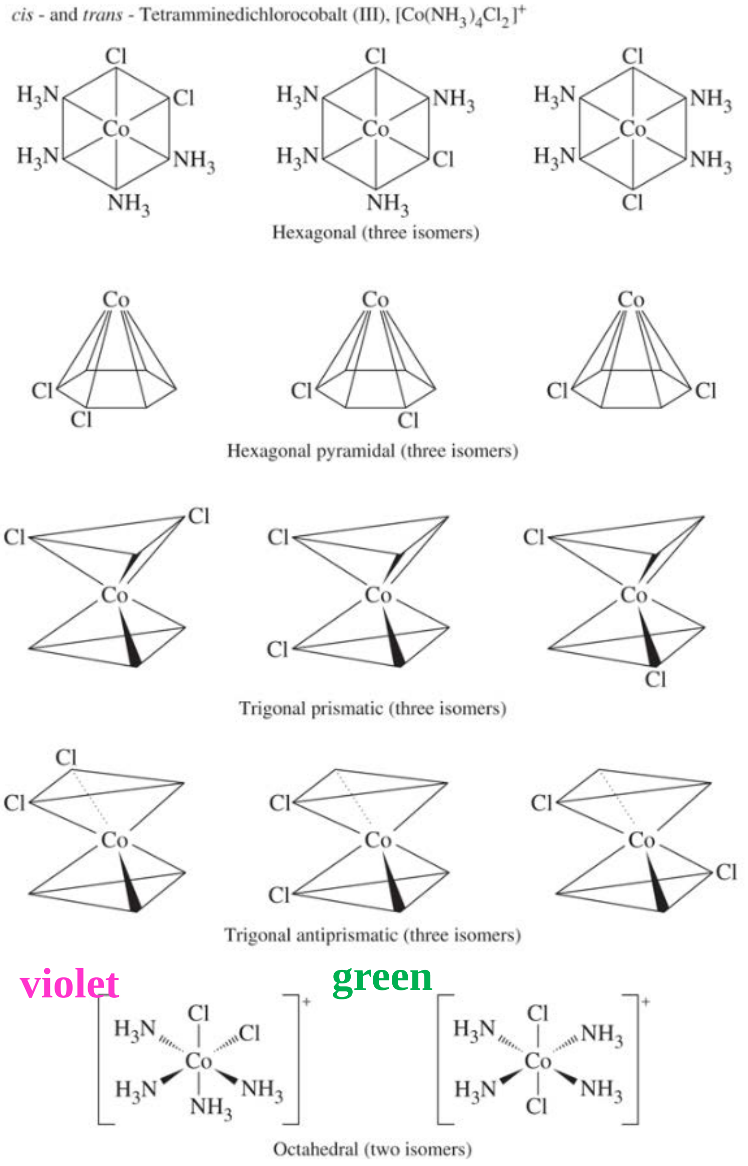
(of other structure)



green

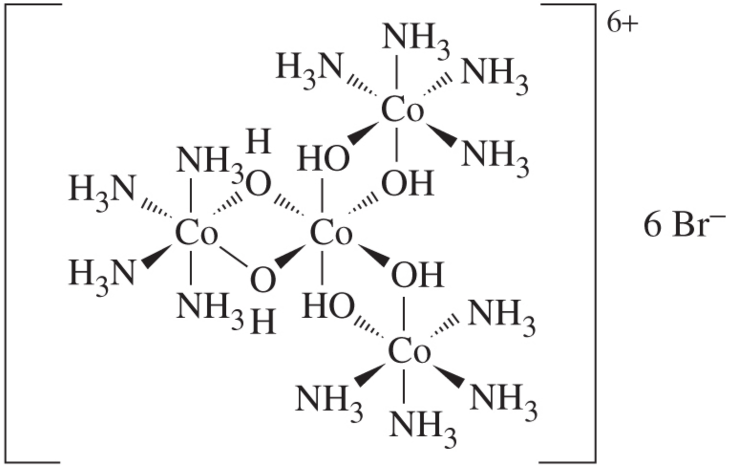


violet



History of Coordination Chemistry

1914, **Werner** finally made a optically active complex not-containing C.

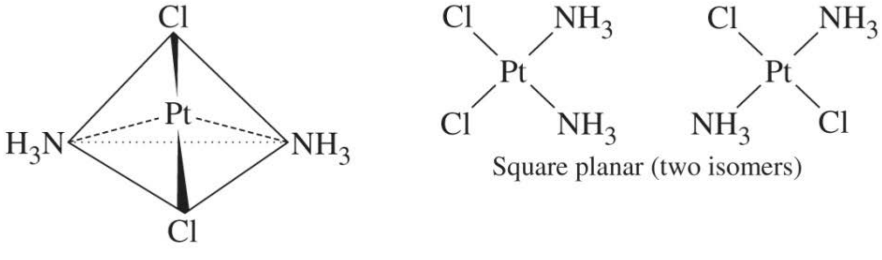


hexol

Alfred Werner (1866-1919)
Nobel prize (1913)

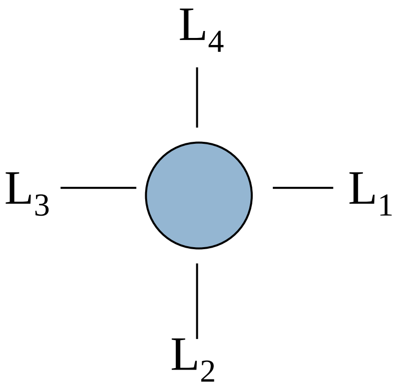
And many other achievement, such as

cis- and *trans*- Diamminedichloroplatinum(II), $[PtCl_2(NH_3)_2]$

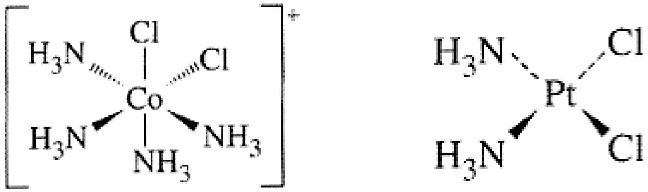


Definitions

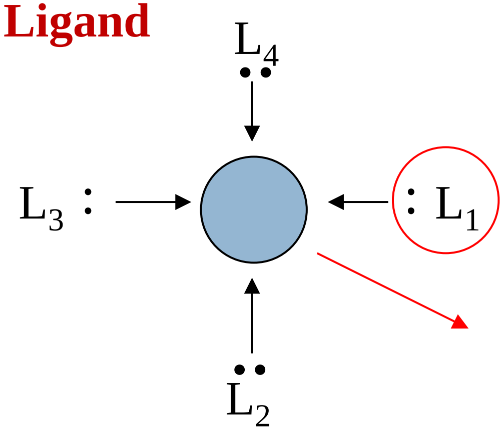
Transition metal complex (Coordination compound)



A metal atom, ion, surrounded by a set of **ligands**. More specifically (or mostly), a transition metal cation surrounded by neutral molecules or anions with a definite geometry.



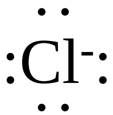
Ligand



Any molecule or ion that has at least one electron pair that can be donated to the central metal atom or ion. (can exist independently)

electron donor, Lewis Base, nucleophile (org. term)

electron acceptor, Lewis acid, electrophile (org. term)

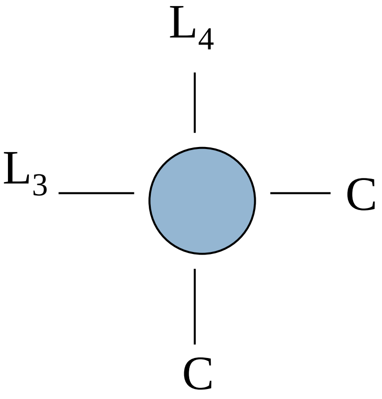


$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}{}^{-}:$

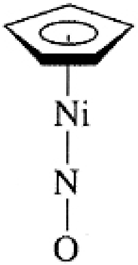
$:NH_3$

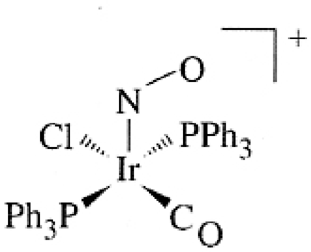
Definitions

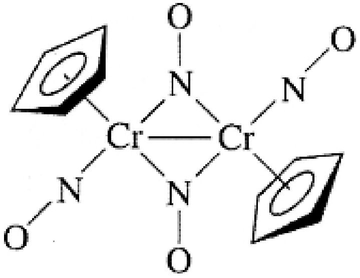
Organometallic compound

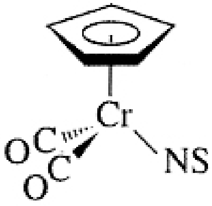


A transition metal surrounded in part or entirely by organic groups in which a carbon atom is directly bonded to the metal ion.









Nomenclature

Types of ligand

monodentate ligands

TABLE 9.2 Common Monodentate Ligands

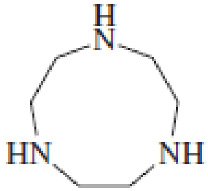
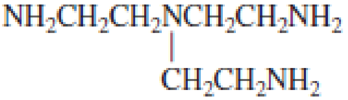
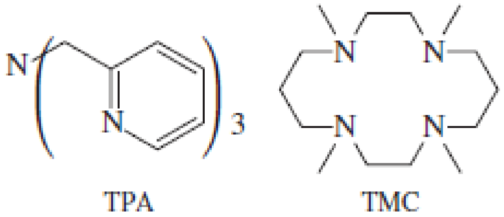
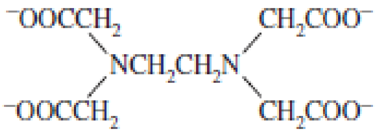
Common Name	IUPAC Name	Formula
hydrido	hydrido	H^-
fluoro	fluoro	F^-
chloro	chloro	Cl^-
bromo	bromo	Br^-
iodo	iodo	I^-
nitrido	nitrido	N^{3-}
azido	azido	N_3^-
oxo	oxido	O^{2-}
cyano	cyano	CN^-
thiocyano	thiocyanato-*S* (S-bonded)	SCN^-
isothiocyano	thiocyanato-*N* (N-bonded)	NCS^-
hydroxo	hydroxo	OH^-
aqua	aqua	H_2O
carbonyl	carbonyl	CO
thiocarbonyl	thiocarbonyl	CS
nitrosyl	nitrosyl	NO^+
nitro	nitrito-*N* (N-bonded)	NO_2^-
nitrito	nitrito-*O* (O-bonded)	ONO^-
methyl isocyanide	methylisocyanide	CH_3NC
phosphine	phosphane	PR_3
pyridine	pyridine (abbrev. py)	C_5H_5N
ammine	ammine	NH_3
methylamine	methylamine	$MeNH_2$
amido	azanido	NH_2^-
imido	azanediido	NH^{2-}

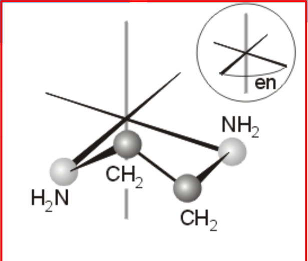
ambidentate

Nomenclature

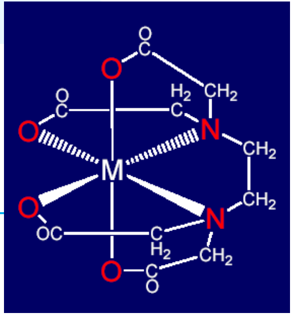
Types of ligand

TABLE 9.3 **Chelating Amines**

Chelating Points	Common Name	IUPAC Name	Abbrev.	Formula
bidentate	ethylenediamine	1,2-ethanediamine	en	$NH_2CH_2CH_2NH_2$
tridentate	diethylenetriamine	1,4,7-triazaheptane	dien	$NH_2CH_2CH_2NHCH_2CH_2NH_2$
		1,3,7-triazacyclononane	tacn	
tetradentate	triethylenetetraamine	1,4,7,10-tetraazadecane	trien	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
	β, β′, β″-triaminotriethylamine	β, β′, β″-tris(2-aminoethyl)amine	tren	 $NH_2CH_2CH_2\underset{CH_2CH_2NH_2}{N}CH_2CH_2NH_2$
	tetramethylcyclam	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane	TMC	
	tris(2-pyridylmethyl) amine	tris(2-pyridylmethyl) amine	TPA	
pentadentate	tetraethylene-pentamine	1,4,7,10,13-pentaazatridecane		$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
hexadentate	ethylenediamine-tetraacetate	1,2-ethanediyl (dinitrilo) tetraacetate	EDTA	



27 Ethylenediamine ligand (en)



multidentate ligands – chelating ligands

Nomen

Types of ligand

multidentate ligands – chelating ligands

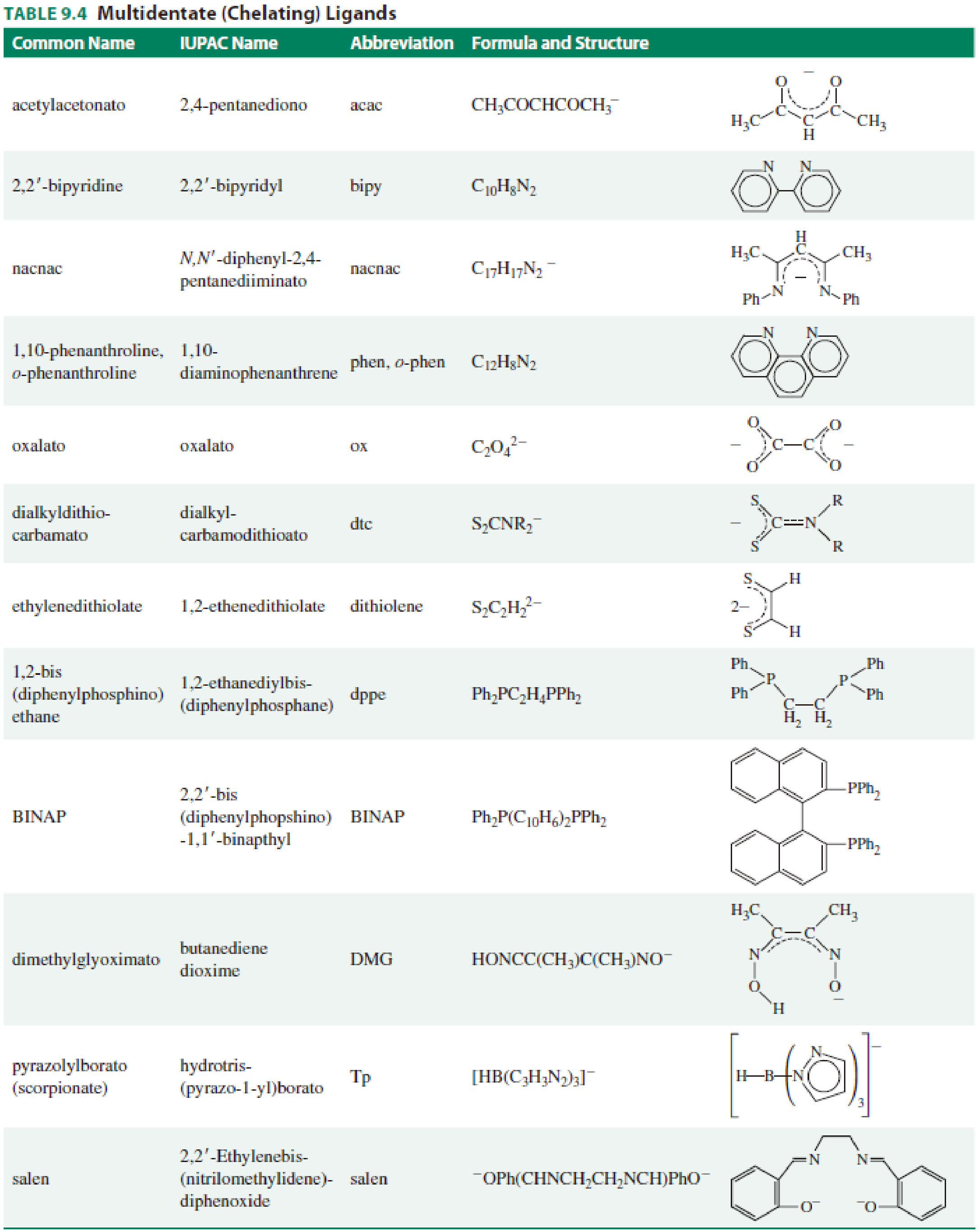
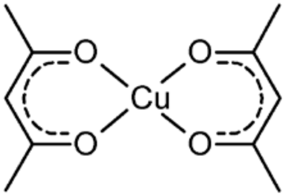
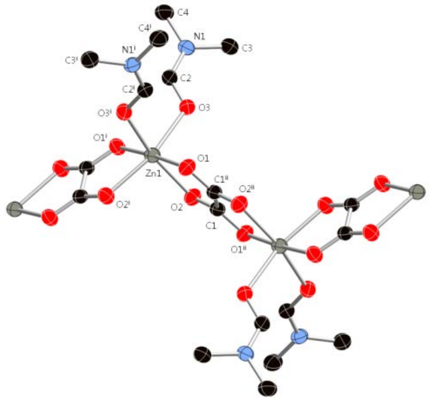
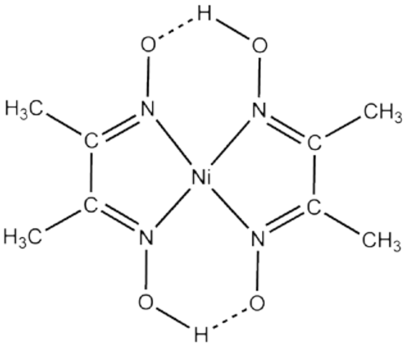


TABLE 9.4 Multidentate (Chelating) Ligands

Common Name	IUPAC Name	Abbreviation	Formula and Structure
acetylacetonato	2,4-pentanediono	acac	$CH_3COCHCOCH_3^-$
2,2′-bipyridine	2,2′-bipyridyl	bipy	$C_{10}H_8N_2$
nacnac	*N,N′*-diphenyl-2,4-pentanediiminato	nacnac	$C_{17}H_{17}N_2^-$
1,10-phenanthroline, *o*-phenanthroline	1,10-diaminophenanthrene	phen, *o*-phen	$C_{12}H_8N_2$
oxalato	oxalato	ox	$C_2O_4^{2-}$
dialkyldithio-carbamato	dialkyl-carbamodithioato	dtc	$S_2CNR_2^-$
ethylenedithiolate	1,2-ethenedithiolate	dithiolene	$S_2C_2H_2^{2-}$
1,2-bis (diphenylphosphino) ethane	1,2-ethanediylbis-(diphenylphosphane)	dppe	$Ph_2PC_2H_4PPh_2$
BINAP	2,2′-bis (diphenylphopshino) -1,1′-binapthyl	BINAP	$Ph_2P(C_{10}H_6)_2PPh_2$
dimethylglyoximato	butanediene dioxime	DMG	$HONCC(CH_3)C(CH_3)NO^-$
pyrazolylborato (scorpionate)	hydrotris-(pyrazo-1-yl)borato	Tp	$[HB(C_3H_3N_2)_3]^-$
salen	2,2′-Ethylenebis-(nitrilomethylidene)-diphenoxide	salen	$^-OPh(CHNCH_2CH_2NCH)PhO^-$







Nomenclature

Nomenclature Rules

1. The cation comes first, followed by anion. (same as in salts)

Ex) $[Ag(NH_3)_2]Cl$ = diamminesilver(I) chloride

$K_3[Fe(CN)_6]$ = potassium hexacyanoferrate(III)

2. Inner sphere complex ion is enclosed in square brackets in the formula.

In the nomenclatures,

the ligands are named before the metal within the coordination sphere.

a space only between cation and anion.

In the formulas, the metal comes first.

Ex) $[Cu(NH_3)_4]SO_4$ = tetraamminecopper(II) sulfate

$[Co(NH_3)_6]Cl_3$ = hexaamminecobalt(III) chloride

3. Prefixes are used for the number of ligands of one kind. If the ligand name contains the prefixes or is complicated, -*is* type prefixes are used.

Ex) $[Co(en)_2Cl_2]F$

= dichlorobis(ethylenediamine)cobalt(III) fluoride

$[Fe(bipy)_3]Cl_2$ = tris(bipyridine)iron(II) chloride

2	di	bis	7	hepta	heptakis
3	tri	tris	8	octa	octakis
4	tetra	terakis	9	nona	nonakis
5	penta	pentakis	10	deca	decakis
6	hexa	hexakis			

Nomenclature

Nomenclature Rules

4. Ligands are named in alphabetical order (not the prefixe).

Ex) $[Co(NH_3)_4Cl_2]^+$ = tetraamminedichlorocobalt(III)

$[Pt(NH_3)BrCl(CH_3NH_2)]$ = amminebromochloromethylamineplatinum(II)

5. Ligand naming:

Ex) Anionic ligands are given an *o* suffix: chloro, fluoro, oxo, sulfato

Neutral ligands retain their usual name: methylamine, bipyridine

Water: aqua, NH_3: ammine (distinguishes from alkylamines)

6. Two systems for designating charge or oxidation nubmer:

(a) Stock system: puts oxidation number of the metal ion in Roman numerals in parenthesis after the name of the metal ion. (more common)

(b) Ewing-Basset system: puts the charge of the total complex ion in parenthesis after the name of the metal ion.

(c) –*ate* to the metal name if the complex ion has an overall (-) charge

Ex) $[Pt(NH_3)_4]^{2+}$ = tetraammineplatinum(II) or tetraammineplatinum(2+)

$[PtCl_4]^{2-}$ = tetrachloroplatinate(II) or tetrachloroplatinate(2-)

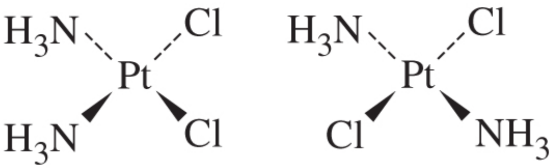
$[PtCl_6]^{2-}$ = hexachloroplatinate(IV) or hexachloroplatinate(2-)

Nomenclature

7. *cis*-, *trans*- (and other prefex for isomers) before the nomenclature in *italics*.

Ex) *cis*-diamminedichloroplatinum(II)

trans-diamminedichloroplatinum(II)

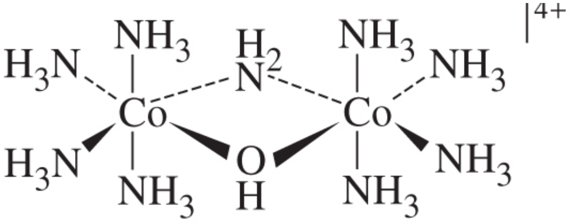


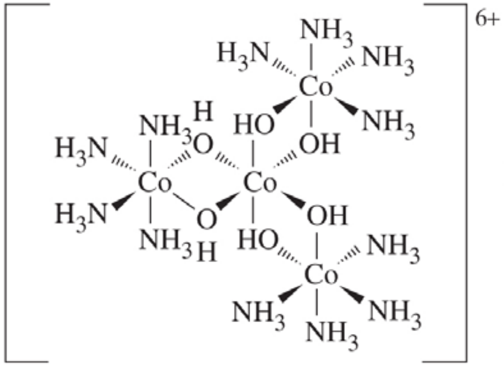
cis *trans*

8. Bridging ligands have the prefix of μ

Ex) $[(NH_3)_4Co(OH)(NH_2)Co(NH_3)_4]^{4+}$ = μ-amido-μ-hydroxobis(tetraaminecobalt(III))

$[Co(Co(NH_3)_4(OH)_2)_3]^{6+}$ = tris(tetraammine-μ-dihydroxocobalt)cobalt(6+)





9. Negatively charged complexes of certain metals use their Latin names:

Fe (iron) = ferrate

Pb (lead) = plumbate

Ag (silver) = argenate

Sn (tin) = stannate

Sb (antimony) = stibate

Au (gold) = aurate

Ex) $[FeCl_4]^-$ = tetrachloroferrate(III) or tetrachloroferrate(1-)

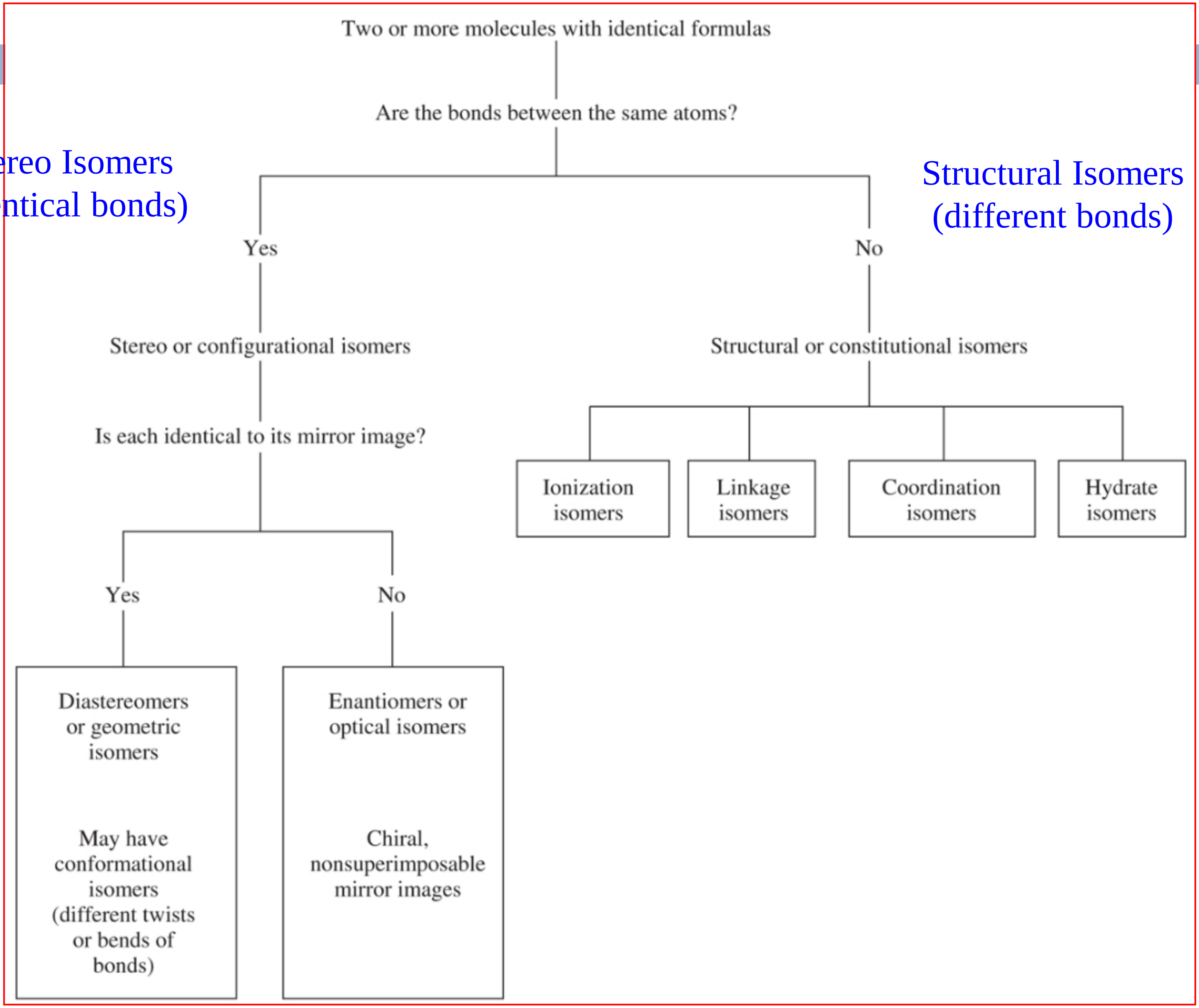
$[Au(CN)_2]^-$ = dicyanoaurate(I) or dicyanoaurate (1-)

Isomerism

Isomers

Stereo Isomers
(identical bonds)

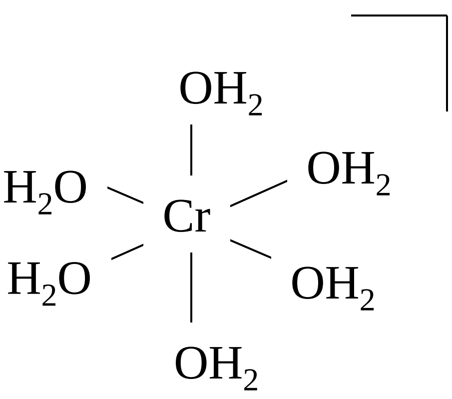
Structural Isomers
(different bonds)



Isomerism

Constitutional Isomers (Structural Isomers)

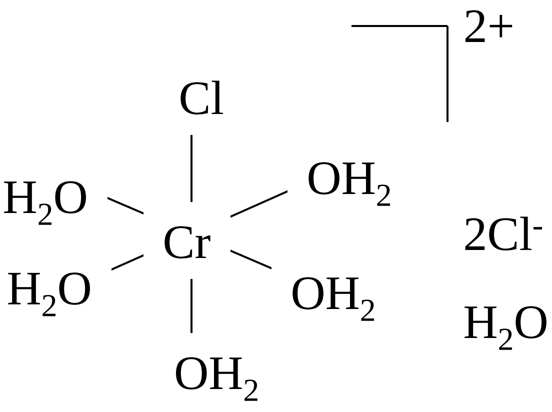
Hydrate isomerism : having water as either a ligand or an added part of the crystal structure



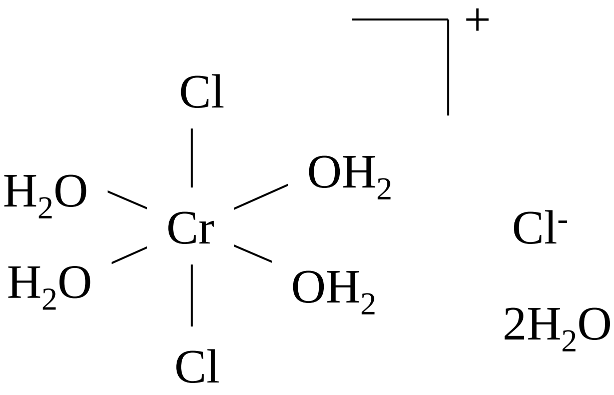
3+

$3Cl^-$

violet



blue-green



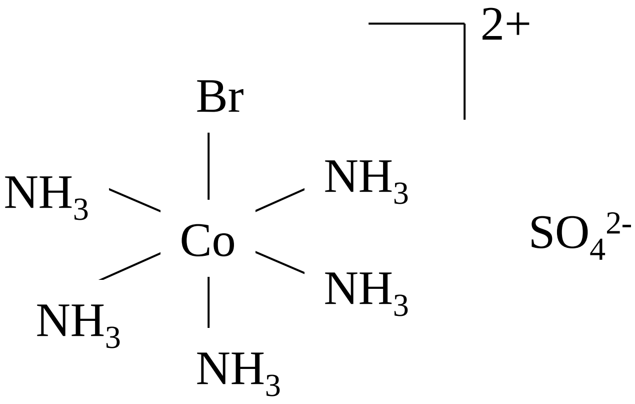
green

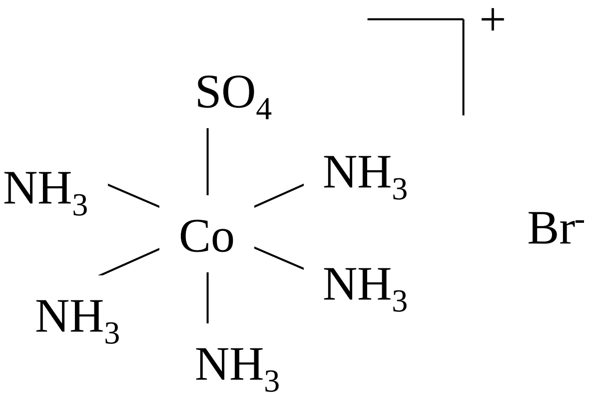
trans-tetraaquadichlorochromium(III) chloridedihydrate

Isomerism

Constitutional Isomers (Structural Isomers)

Ionization isomerism : exchange of ions inside and outside coordination sphere





$[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Br_2]Cl{\bullet}H_2O$

$[Co(NH_3)_5SO_4]NO_3$ and $[Co(NH_3)_5NO_3]SO_4$

Coordination isomerism : occurs in compound containing both anion and cation complexes

$[Co(en)_3]^{3+}[Cr(CN)_6]^{3-}$

$[Cr(en)_3]^{3+}[Co(CN)_6]^{3-}$

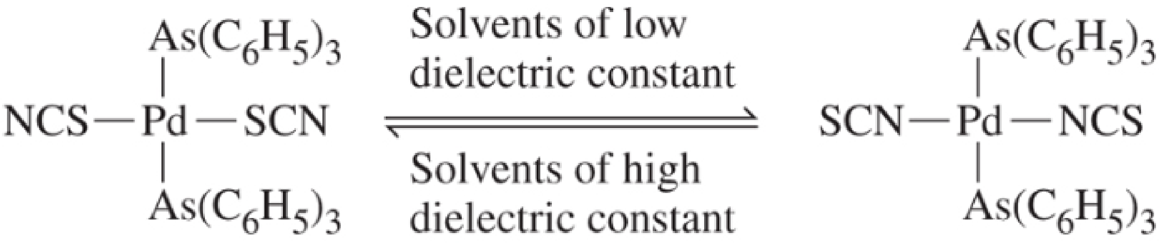
$[Pt(NH_3)_4]^{2+}[PtCl_6]^{2-}$

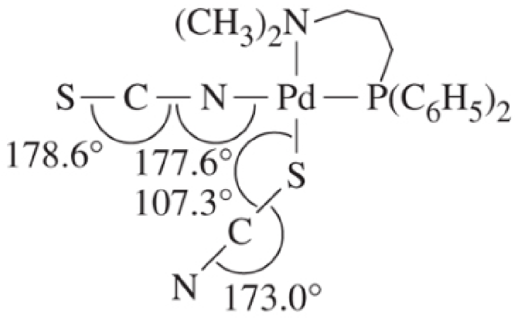
$[Pt(NH_3)_4Cl_2]^{2+}[PtCl_4]^{2-}$

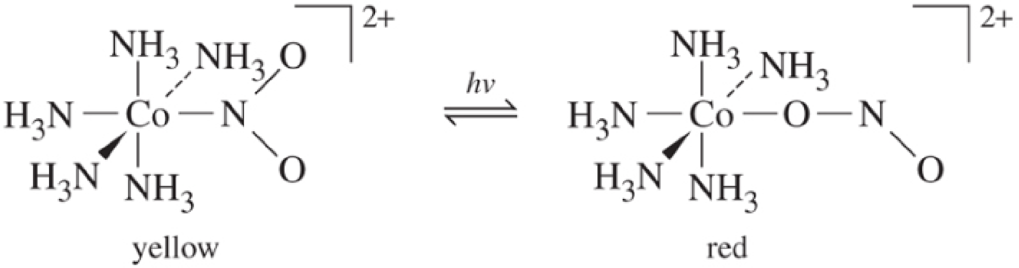
Isomerism

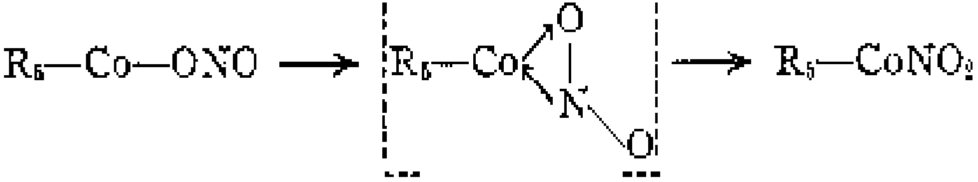
Constitutional Isomers (Structural Isomers)

Linkage (ambidentate) isomerism : occurs in compounds containing ambidentate ligands

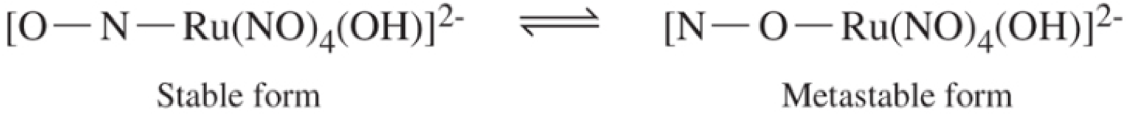








Intramolecular rearrangement (kinetic and ^{18}O labeling expmt)



$$[O—N—Ru(NO)_4(OH)]^{2-} \rightleftharpoons [N—O—Ru(NO)_4(OH)]^{2-}$$

Stable form

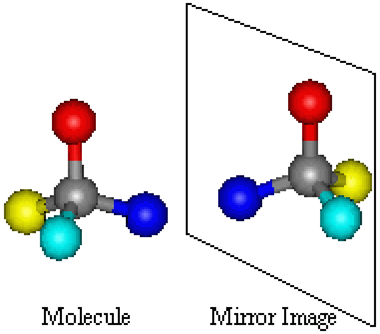
Metastable form

Isomerism

Stereoisomers

Optical isomerism : when mirror image is nonsuperimposiable

Geomerical isomerism : steroisomerismin except for the optical isomerism

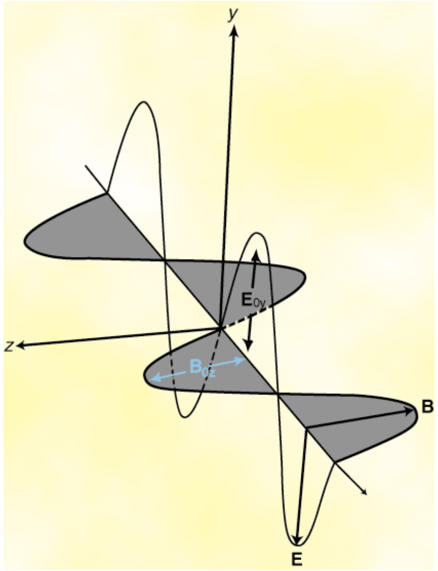


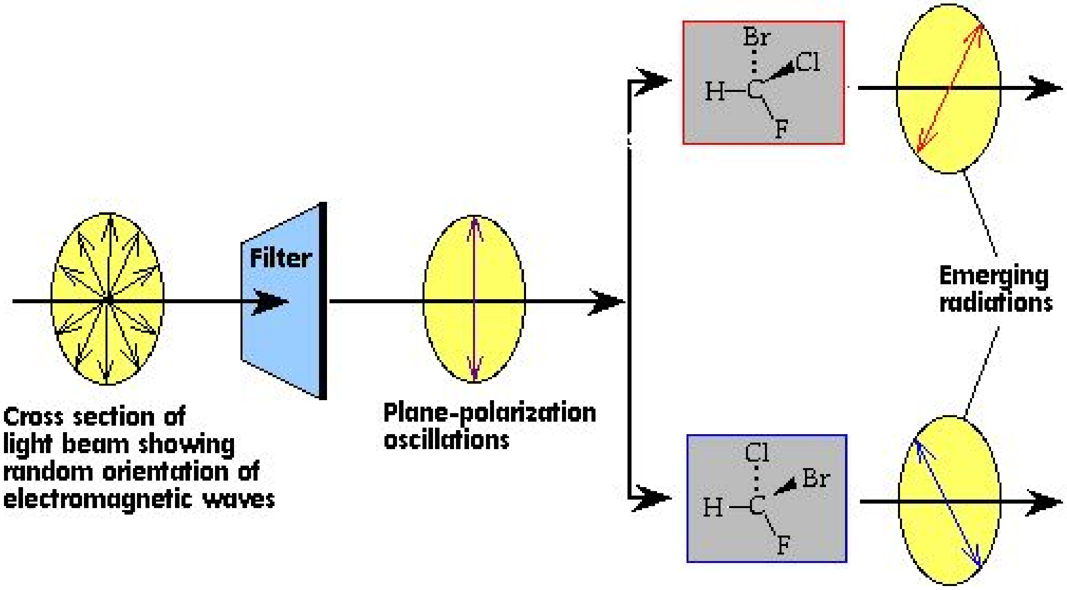
Chiral complex: complex not superimposable on its own mirror image

Optically active: rotating the plane-polarized light

Enantiomers: mirror-image partners

Molecules with S_n → no chirality ($i = S_2$, $\sigma = S_1$)

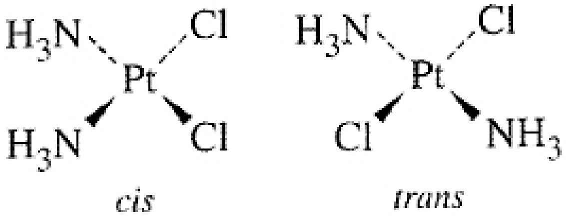




Isomerism

Stereoisomers

CN=4



[$PtBrCl(PR_3)_2$]

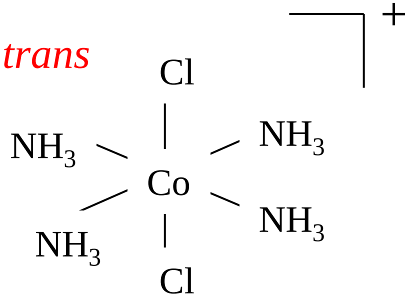
^{31}P NMR 1 peak

^{31}P NMR 2 peaks

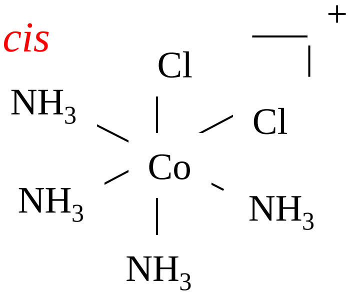
CN=6

MX_4Y_2

trans

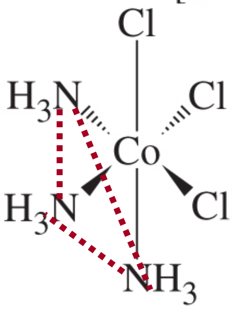


cis

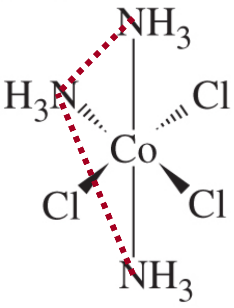


MX_3Y_3

[$Co(NH_3)_3Cl_3$]

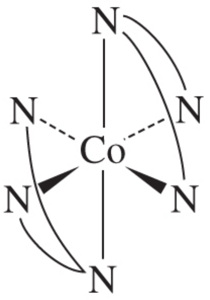


fac (facial)

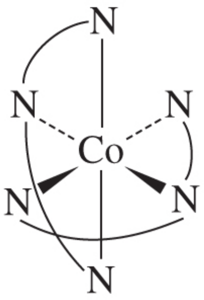


mer (meridional)

[$Co(dien)_2$]$^{3+}$



fac (facial)



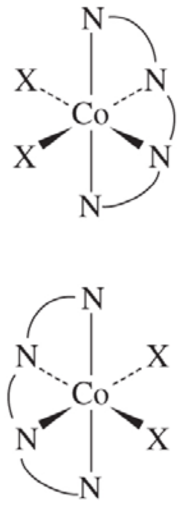
mer (meridional)

Isomerism

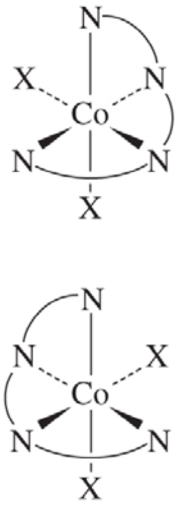
Stereoisomers

CN=6 (cont’d)

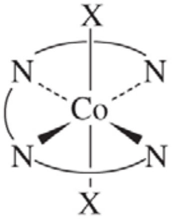
enantiomer pair



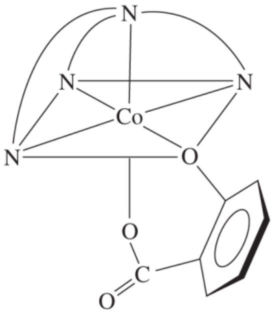
α
No coplanar rings



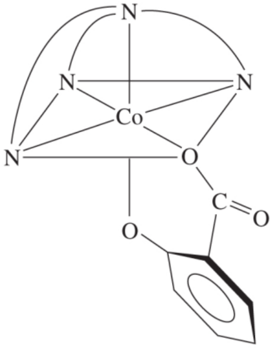
β
Two coplanar rings



trans
Three coplanar rings



COO⁻ *trans* to tertiary N

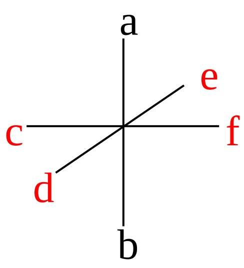


COO⁻ *cis* to tertiary N

many other geometrical iosomers….

Isomerism

CN=6 (cont’d) Isomers of Mabcdef (O_h)



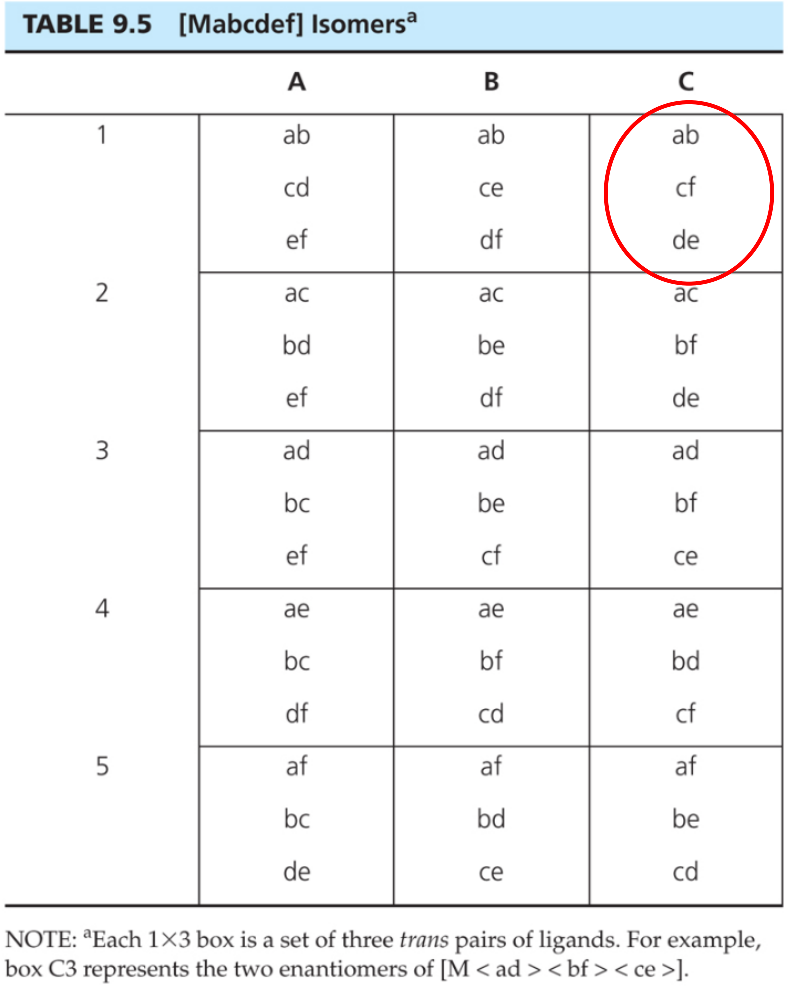
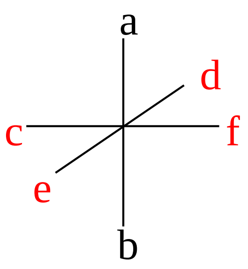


TABLE 9.5 [Mabcdef] Isomers[a]

	A	B	C
1	ab cd ef	ab ce df	ab cf de
2	ac bd ef	ac be df	ac bf de
3	ad bc ef	ad be cf	ad bf ce
4	ae bc df	ae bf cd	ae bd cf
5	af bc de	af bd ce	af be cd

NOTE: [a]Each 1×3 box is a set of three *trans* pairs of ligands. For example, box C3 represents the two enantiomers of [M < ad > < bf > < ce >].



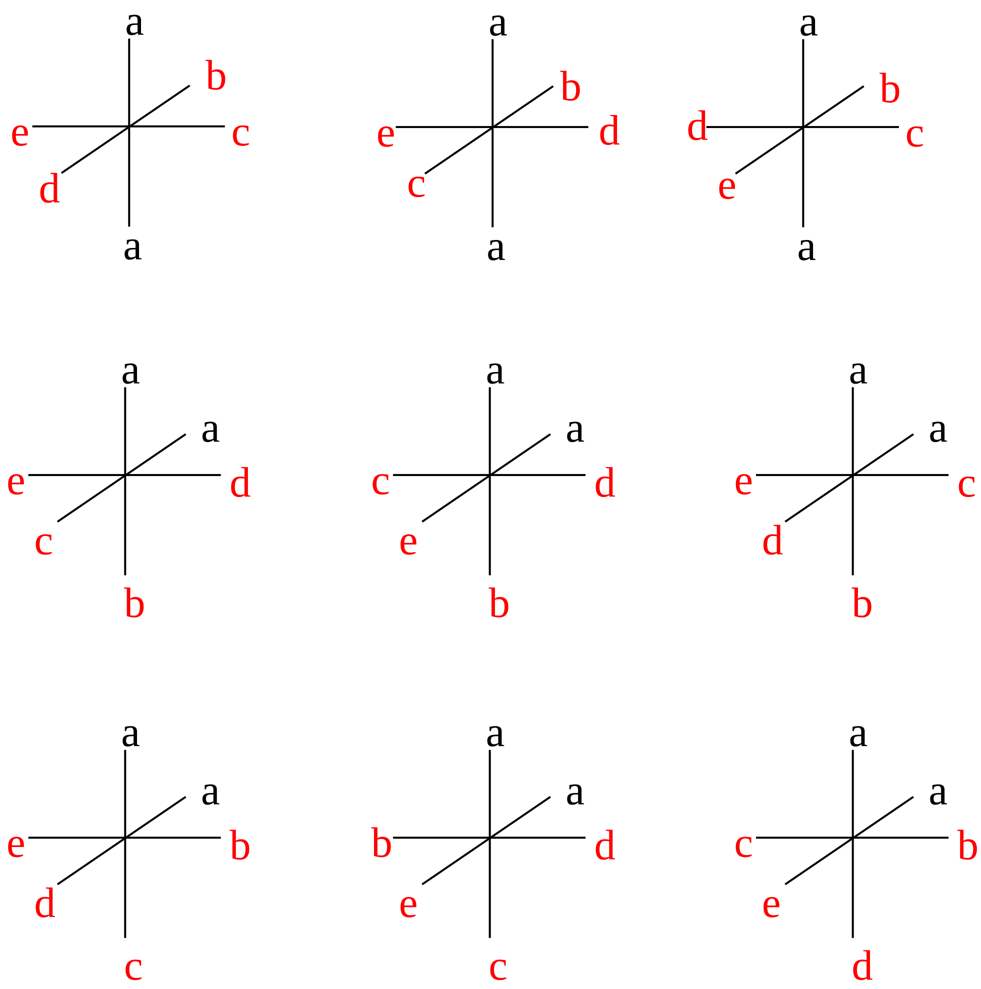
Mirror image

Total = 30

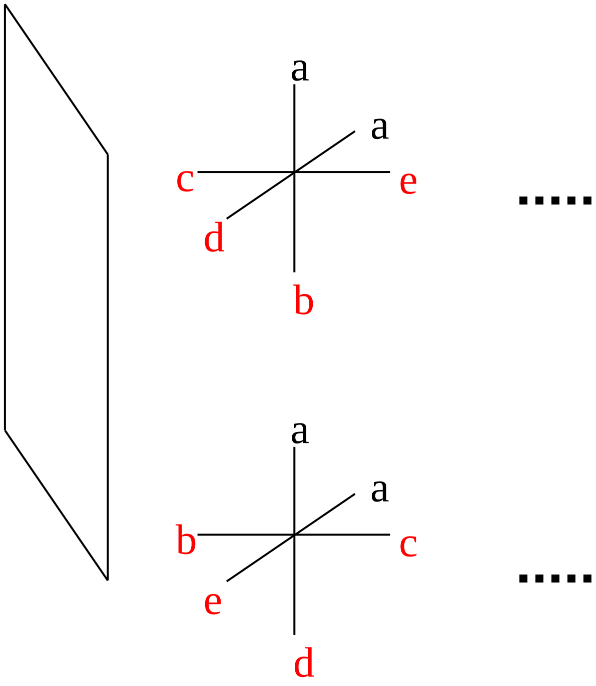
Isomerism

CN=6 (cont'd)

Isomers of Ma_2bcde (O_h)



15 stereoisomers
(6 pairs of
enantiomers)



Isomerism

Stereoisomers

CN=6 (cont’d)

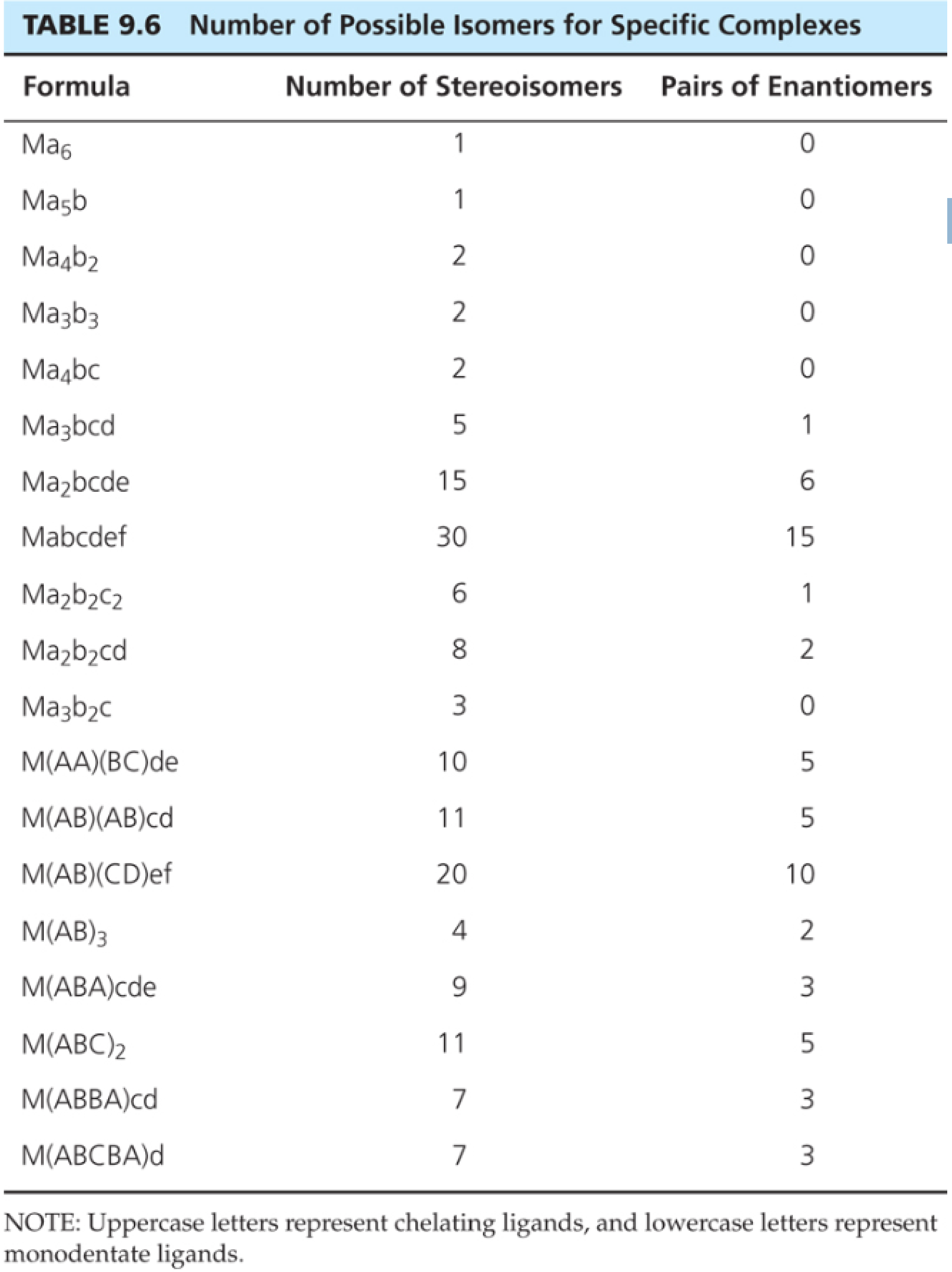


TABLE 9.6 Number of Possible Isomers for Specific Complexes

Formula	Number of Stereoisomers	Pairs of Enantiomers
Ma_6	1	0
Ma_5b	1	0
Ma_4b_2	2	0
Ma_3b_3	2	0
Ma_4bc	2	0
Ma_3bcd	5	1
Ma_2bcde	15	6
Mabcdef	30	15
$Ma_2b_2c_2$	6	1
Ma_2b_2cd	8	2
Ma_3b_2c	3	0
M(AA)(BC)de	10	5
M(AB)(AB)cd	11	5
M(AB)(CD)ef	20	10
$M(AB)_3$	4	2
M(ABA)cde	9	3
$M(ABC)_2$	11	5
M(ABBA)cd	7	3
M(ABCBA)d	7	3

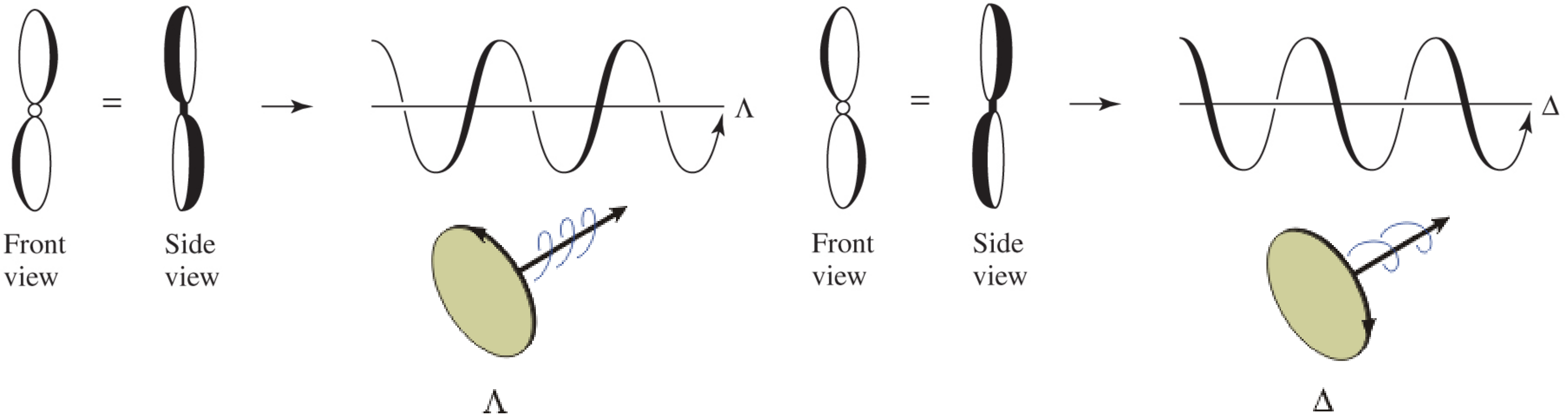
NOTE: Uppercase letters represent chelating ligands, and lowercase letters represent monodentate ligands.

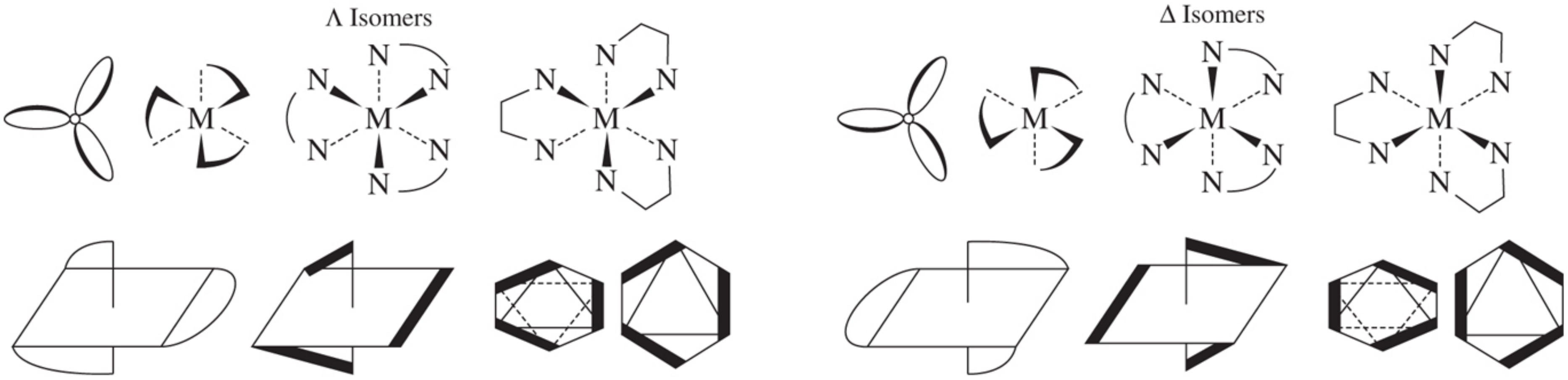
Isomerism

Stereoisomers

Optical isomers of octahedral complexes with chelate rings (Λ, Δ)

Handedness

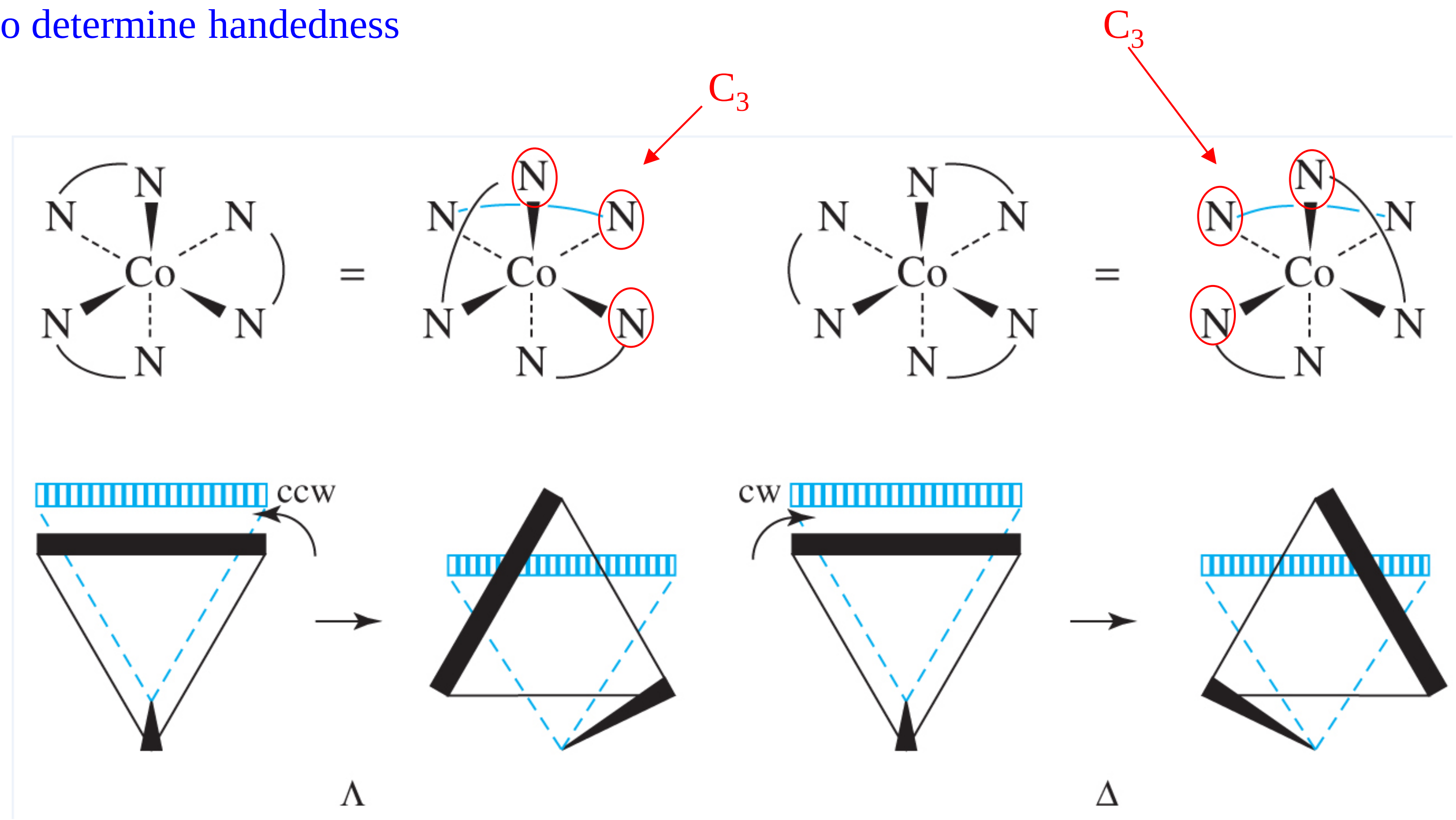




Isomerism

Optical isomers of octahedral complexes with chelate rings (Λ, Δ)

Procedure to determine handedness

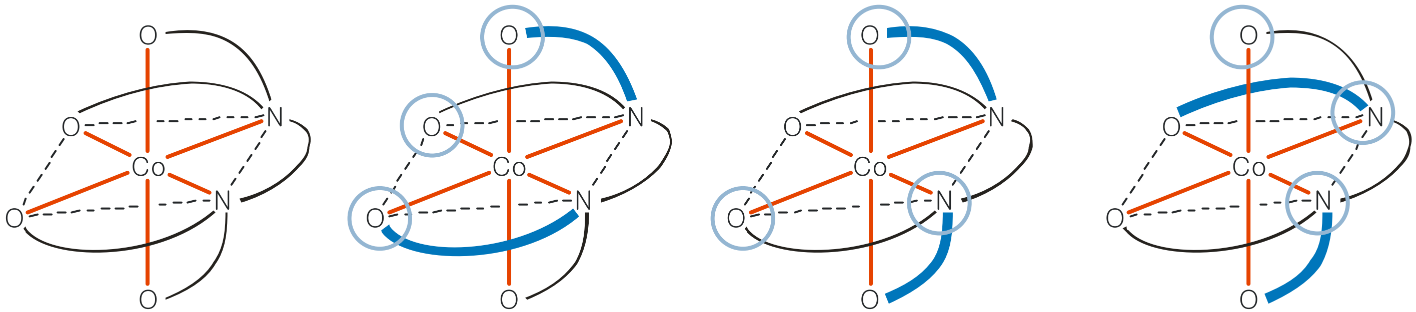


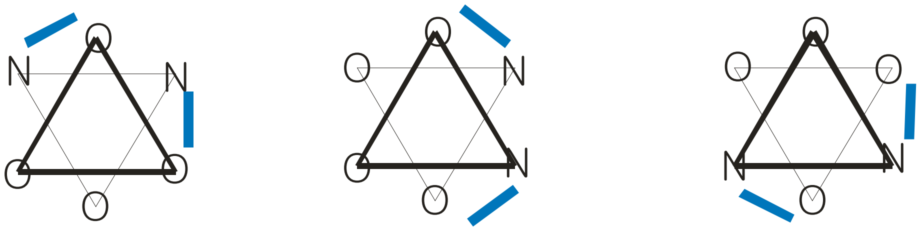
Isomerism

Stereoisomers

Optical isomers of octahedral complexes with chelate rings (Λ, Δ)

$Co(EDTA)^-$



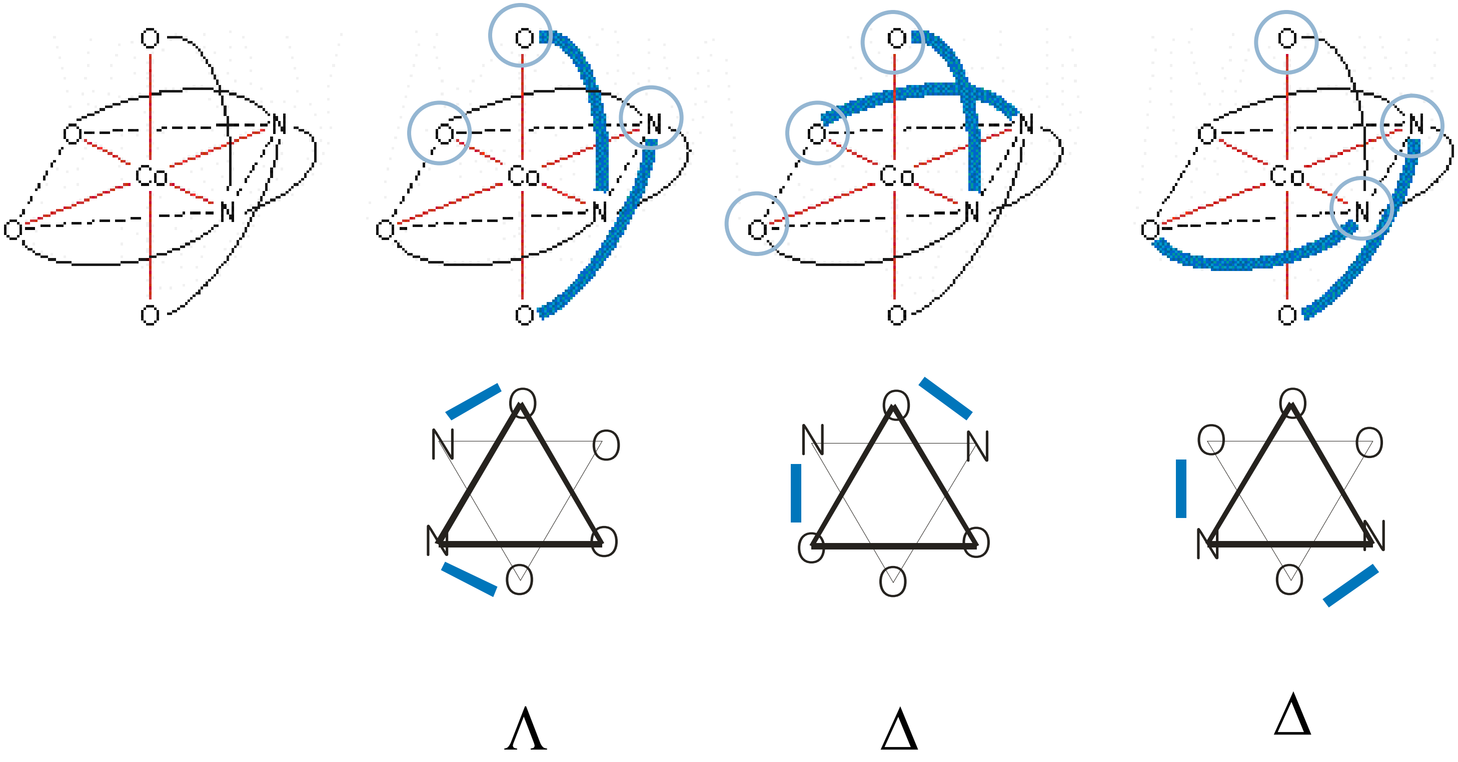


Λ Δ Λ

ΛΔΛ-(ethylenediaminetetraacetato)cobaltate(III)
= ΛΛΔ- "
= ΔΛΛ- "

Optical isomers of octahedral complexes with chelate rings (Λ, Δ)

Co(EDTA)$^-$



ΛΔΔ-(ethylenediaminetetraacetato)cobaltate(III)
= ΔΛΔ- "
= ΔΔΛ- "

Isomerism

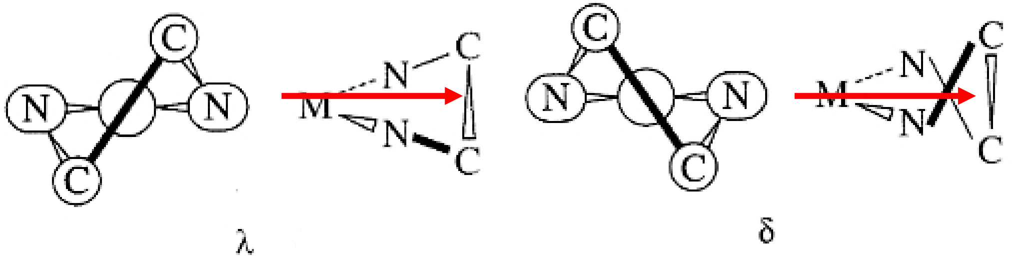
Stereoisomers

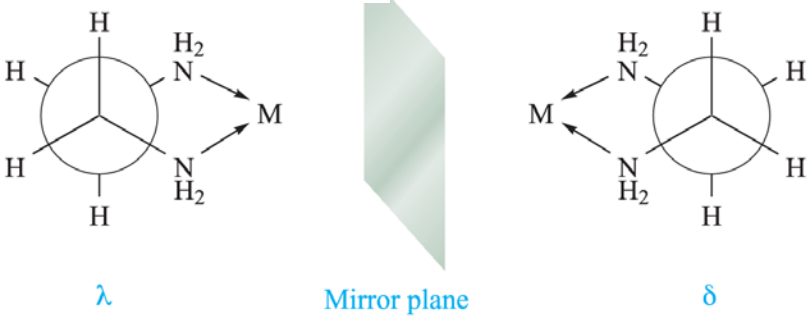
Optical isomerism arising from ligand ring conformation (λ, δ)

Many chelate rings are not planar, they can have different conformations in different molecules.

Ex) ethylenediamine (en) :
1st line – conneting atoms bonded to the metal
2nd line – conneting two carbon atoms

rotation of the 2nd line: counterclockwise → λ
rotation of the 2nd line: clockwise → δ





Ex) $[Co(en)_3]^{3+}$

$\Delta\lambda\lambda\lambda$-$[Co(en)_3]^{3+}$ is more stable than $\Delta\delta\delta\delta$-$[Co(en)_3]^{3+}$ in calculation
$\Lambda\delta\delta\delta$-$[Co(en)_3]^{3+}$ is more stable than $\Lambda\lambda\lambda\lambda$-$[Co(en)_3]^{3+}$ in calculation

actually, in solution λ ←→ δ intercoversion

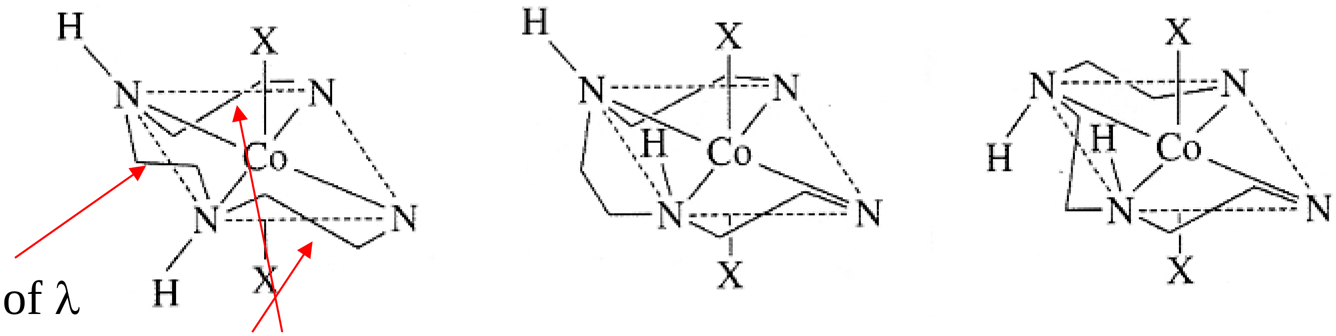
in soln, δδλ is most abundant in Λ form

Isomerism

Stereoisomers

Optical isomerism arising from ligand ring conformation (λ, δ)

Chiral structures of *trans*-$[CoX_2(trien)]^+$



only 1 choice of λ

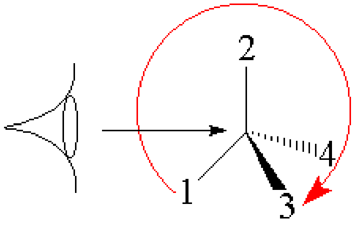
δδ δλ λλ

Isomerism

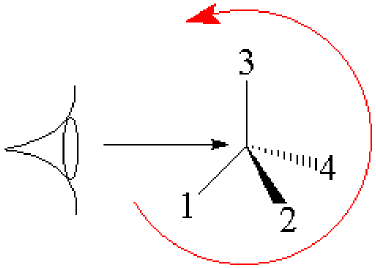
Stereoisomers

Optical isomerism arising from the chiral center of ligands (R, S)

Cahn-Ingold-Prelog Rules



R (rectus)



S (sinister)

Ligand precedence rules

1. Ligands of the higher atomic number precede those with lower ones, e.g. Br precedes Cl (Br>Cl).

2. For ligands with the same type of atoms linked to the center C, the precedence is determined based on the atomic numbers of ligands in the next sphere, e.g. ligand with C-O sequence precedes C-C. If no difference is detected, the determination is based on the distinction in the next spheres, and search is continued until the difference is detected.

3. The coordination number of non-hydrogen atoms is assumed to be 4, i.e. atoms bonded with multiple bonds are considered to be bonded to multiple atoms, e.g. carbonyl carbon is treated as if it was bonded to two oxygen atoms, and carboxyl carbon as if it was bonded to three oxygens (these are then called phantom atoms). Ligand duplication is also necessary in the cases of cyclic systems.

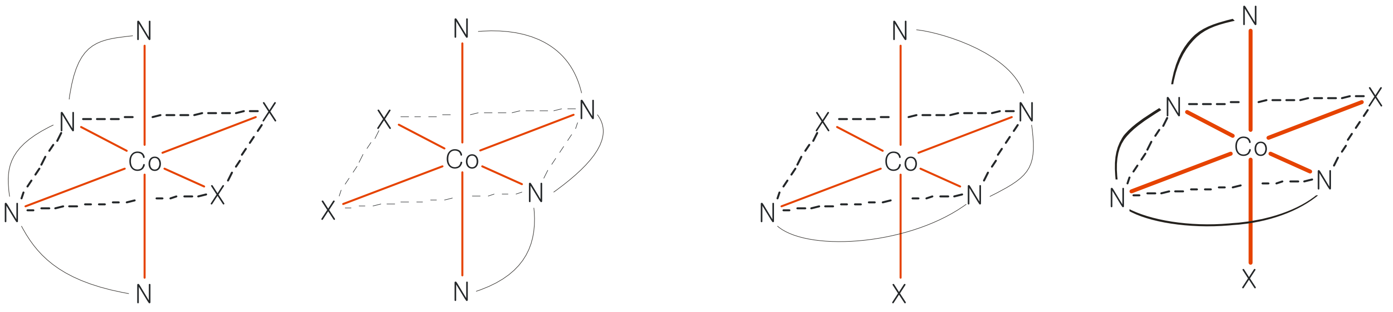
4. Ligands of the same atomic number, but a higher atomic mass precede those with a lower atomic mass, e.g. D precedes H (D>H). This criterion applies only after the previous ones were exhausted.

5. For compounds where only configurational (not constitutional) differences between ligands are detected, the following rules apply: a. The olefinic ligand that has the chiral center and another ligand on the same side of the double bond (cis) precedes the one with the trans-configuration. b. Ligands with R,R or S,S precede R,S or S,R. c. R precedes S.

Isomerism

Stereoisomers

Ex) $[CoX_2(trien)]^+$



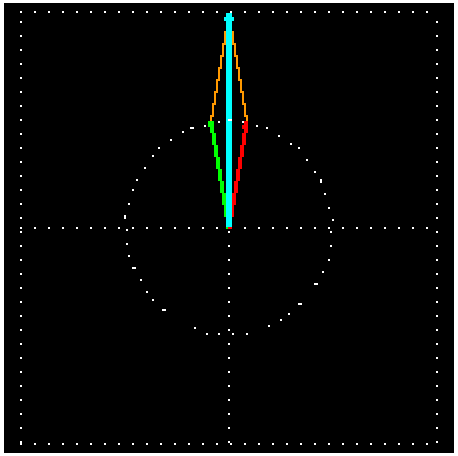
geometrical	α		β	
optical (chirality on chelate-ring conformation)	Λ	Δ	Λ	Δ
optical (chirality on ligands)	RR	SS	SS	RR

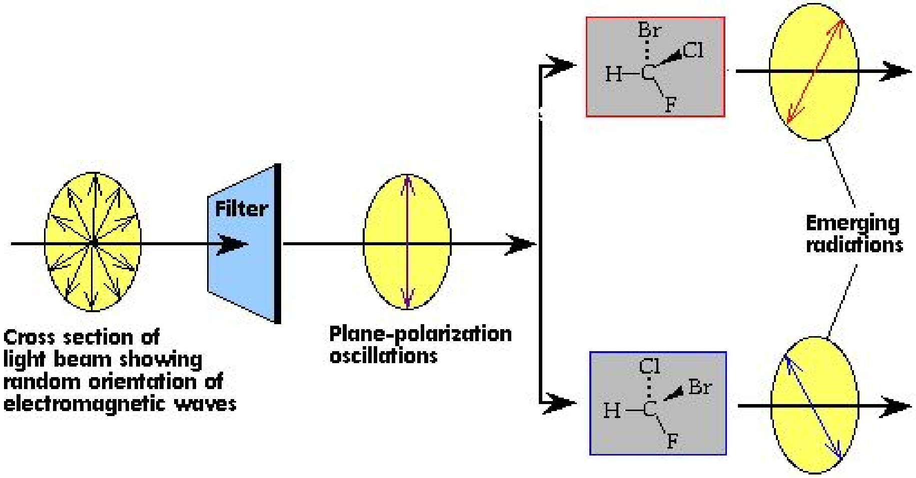
Separation and Identification of Isomers

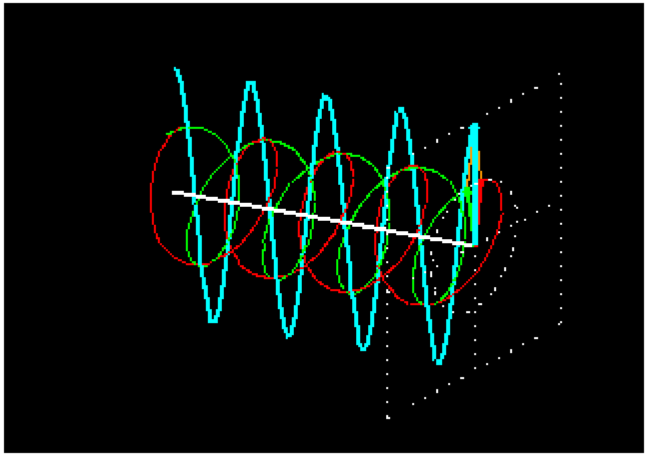
Separation

1. Geometric isomers can be separated by fractional crystallization with different counterions.-
   - Due to the slightly different shapes of the isomers.
   - The ‘fit’ of the counterion can greatly influence solubility.
   - Solubility is the lowest when the positive and negative charges have the same size and magnitude of charges (Basolo).
2. Optical isomers: Separations are performed with chiral counterions.
   - The resulting physical properties will differ allowing separation.

Identification of optical isomers (CD and ORD)



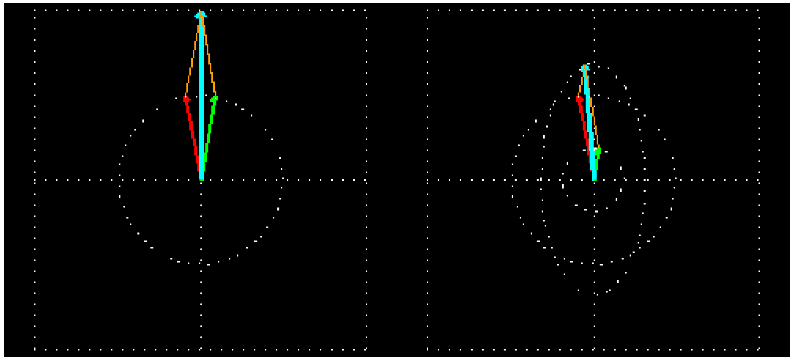




Plane-polarized light
= right circularly polarized light
+ left circularly polarized light

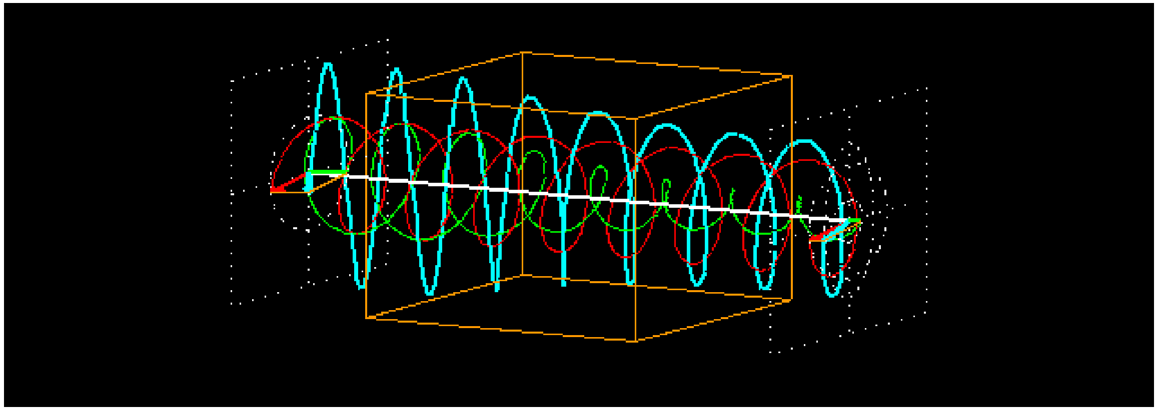
http://www.enzim.hu/~szia/cddemo/edemo0.htm

Identification of optical isomers (CD and ORD)



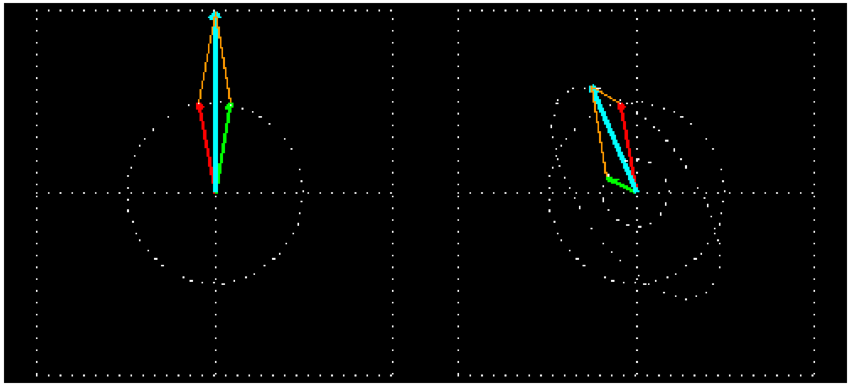
Circular dichroism (CD) is the absorption difference between left and right circularly polarized light at a given wavelength. => absorptive

$$\boxed{\text{Circular dichroism} = \varepsilon_\mathrm{l} - \varepsilon_\mathrm{r}}$$



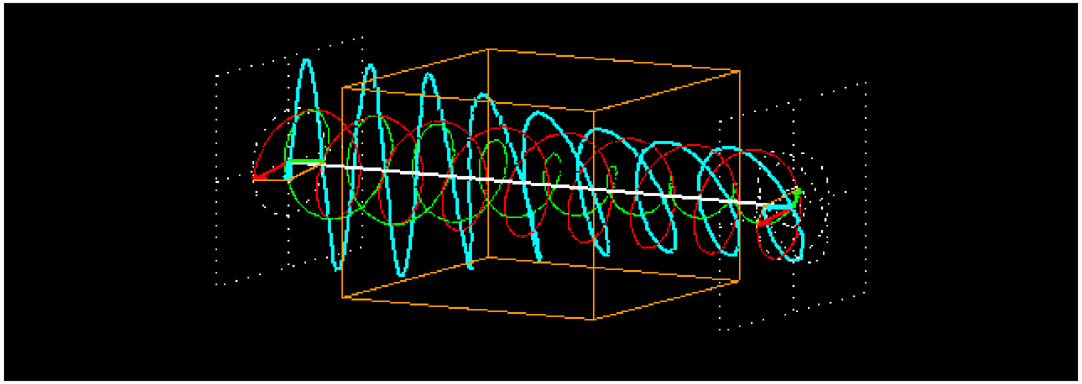
$$\varepsilon_l \neq \varepsilon_r,\ \ n_l = n_r$$

Identification of optical isomers (CD and ORD)



Optical rotatory dispersion (ORD) : The variation of optical rotation as a function of wavelength. (Cotton effect for a single band) => dispersive

$$\boxed{\alpha = \frac{\eta_l - \eta_r}{\lambda}}$$



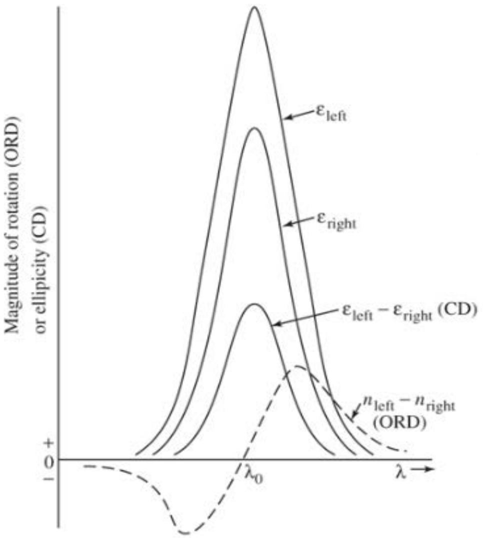
Cotton effect: In a wavelength region where the light is absorbed, the absolute magnitude of the optical rotation at first varies rapidly with wavelength, crosses zero at absorption maxima and then again varies rapidly with wavelength but in opposite direction.

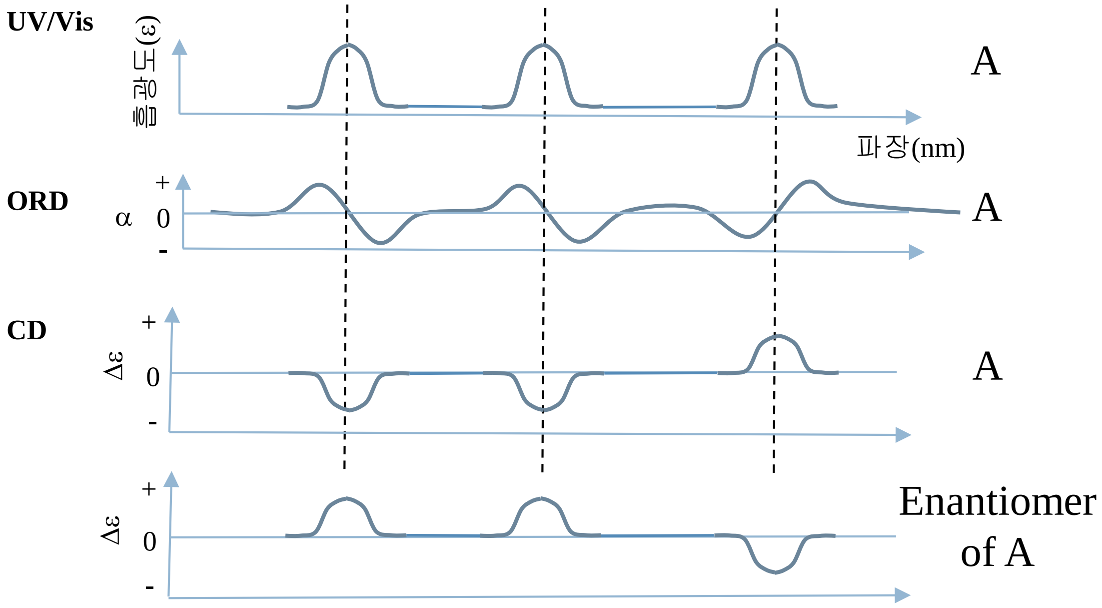
$\varepsilon_l \neq \varepsilon_r$, $n_l \neq n_r$ (Almost all the chiral molecules)

Isomerism

Separation and Identification of Isomers

Identification of optical isomers (CD and ORD)

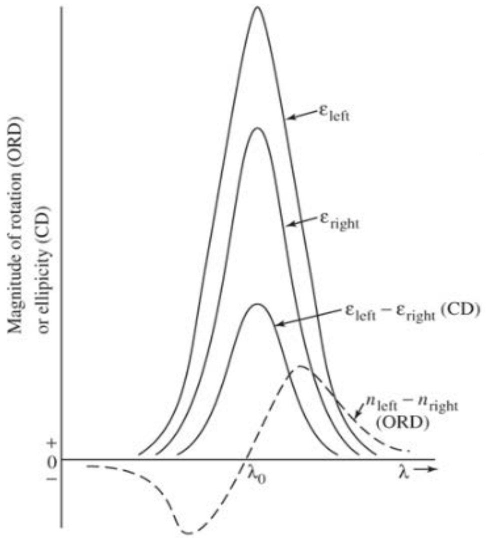


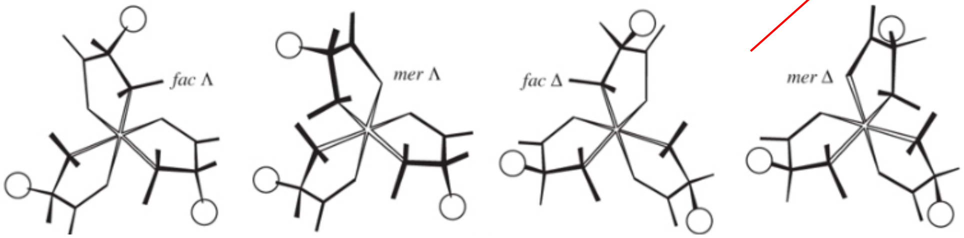


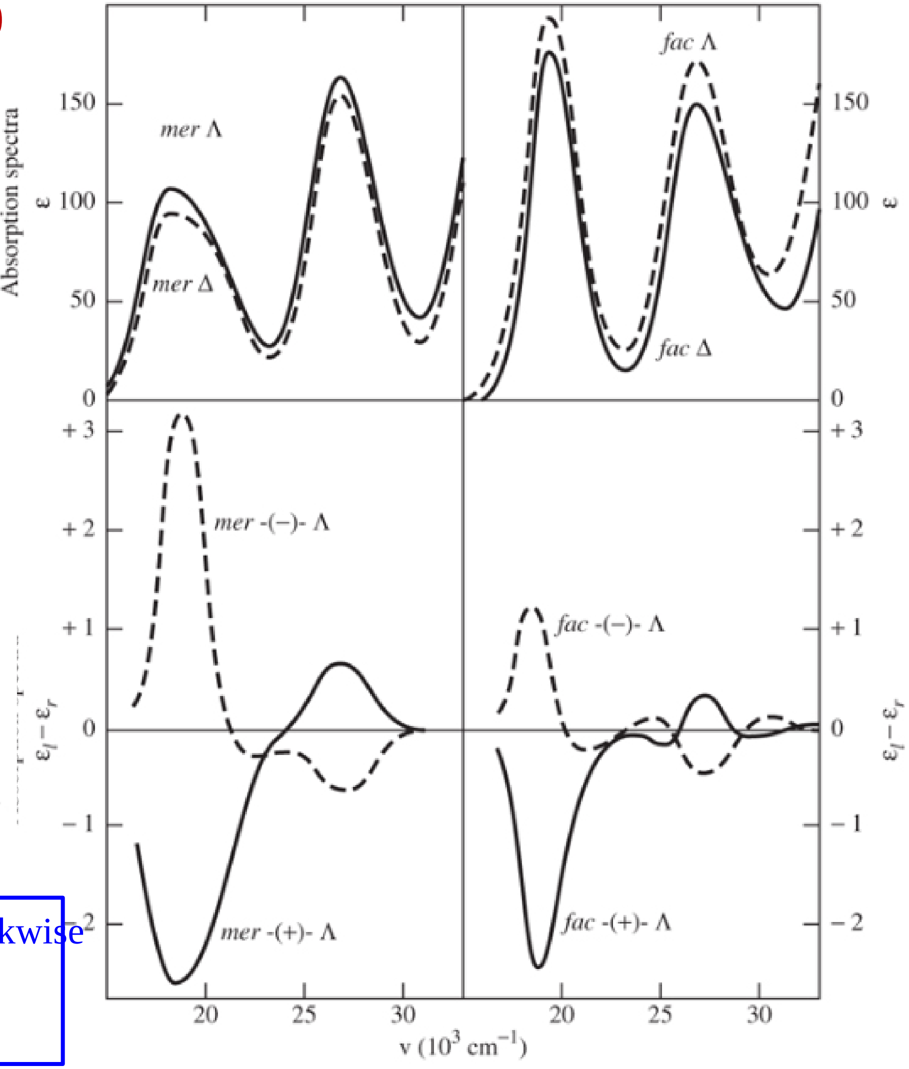
Isomerism

Separation and Identification of Isomers

Identification of optical isomers (CD and ORD)







Dextrorotation (d- or (+)-): rotating plane polarized light clockwise
Levorotation (l- or (-)-): counterclockwise

전자 배치

전이 금속

K: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 = [Ar]4s^1$

Ca: $[Ar]4s^2$

Sc: $[Ar]4s^2 3d^1$

Ti: $[Ar]4s^2 3d^2$

⋮

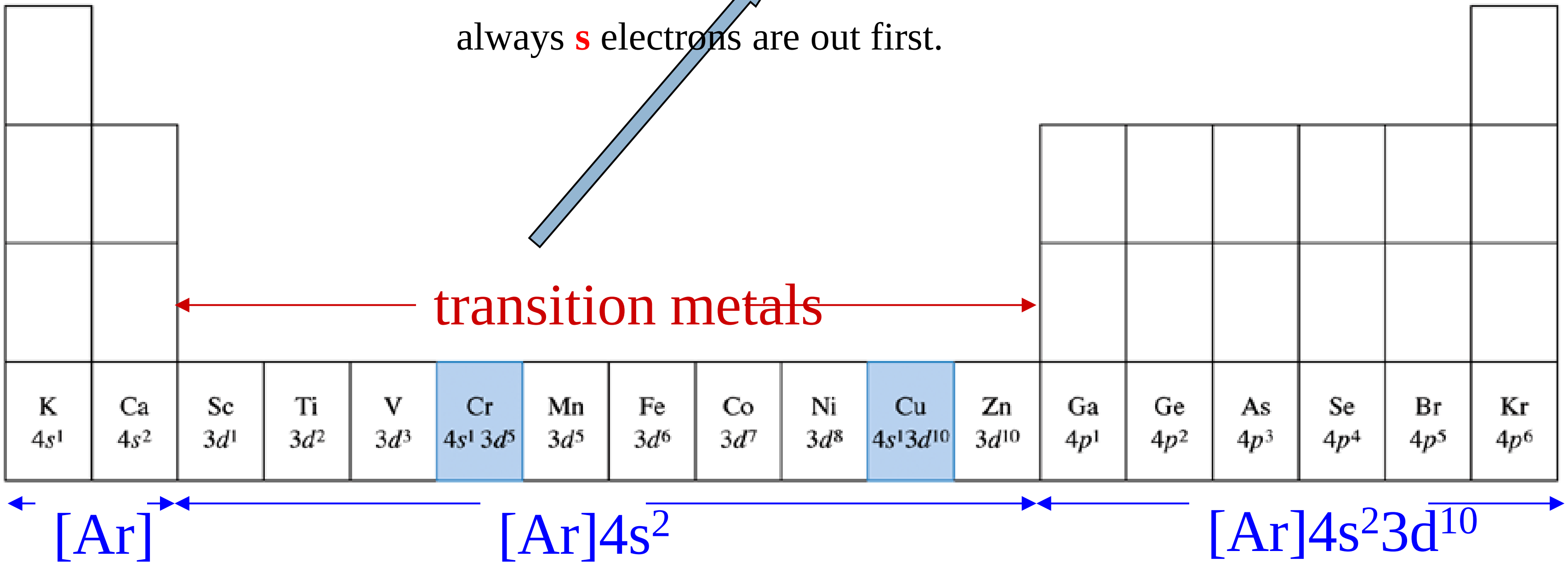
Cations

K^+ : [Ar]

Ca^+ : $[Ar]4s^1$

V^{2+} : $[Ar]3d^3$
Mn^{2+} : $[Ar]3d^5$
Co^{2+} : $[Ar]3d^7$
Cu^{2+} : $[Ar]3d^9$
Cr^{2+} : $[Ar]3d^4$
Fe^{2+} : $[Ar]3d^6$
Ni^{2+} : $[Ar]3d^8$
Zn^{2+} : $[Ar]3d^{10}$

always s electrons are out first.



transition metals

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
$4s^1$	$4s^2$	$3d^1$	$3d^2$	$3d^3$	$4s^1 3d^5$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$4s^1 3d^{10}$	$3d^{10}$	$4p^1$	$4p^2$	$4p^3$	$4p^4$	$4p^5$	$4p^6$

[Ar]

$[Ar]4s^2$

$[Ar]4s^2 3d^{10}$

Coordination Numbers and Structures

Two most important concepts in transition-metal complex chemistry

Oxidation states of metals

Coordination numbers and geometries

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
≤0			o	o	o	o	o	o	o	
+1			o	o	o	o	o	o	**O**	
+2		o	**O**	o	**O**	**O**	**O**	**O**	**O**	**O**
+3	**O**	o	o	**O**	o	**O**	**O**	o	o	
+4		**O**	o	o	**O**	o	o	o		
+5			**O**	o	o	△	o			
+6				**O**	o	o				
+7					**O**					

O : most common

Coordination Numbers and Structures

Two most important concepts in transition-metal complex chemistry

Oxidation states of metals

Coordination numbers and geometries

Factors

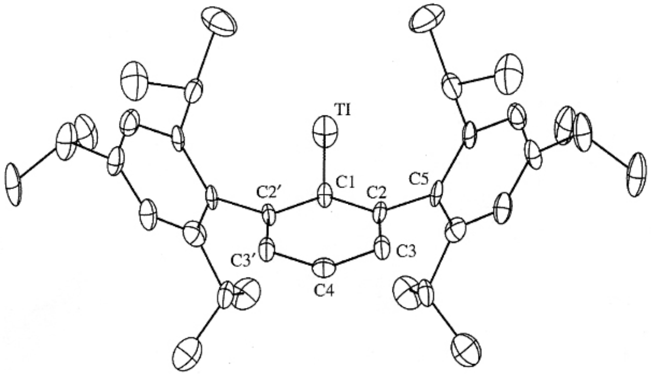
1. Number of bonds
2. VSEPR arguments
3. Occupancy of d-orbitals (LFT)
4. Steric inference by large ligands
5. Crystal packing effects

CN	Geometries
1	rare
2	Linear (rare)
3	Trigonal-plane
4	**Tetrahedron,** Square-plane
5	Trigonal bipyramid, Square pyramid
6	**Octahedron**, Triogonal prism
7	Pentagnal bipyramid, Capped trigonal prism, Capped octahedron
8≤	Known up to 16 CN

Coordination Numbers and Structures

CN = 1, 2, 3

CN = 1 : very rare



Tl(I): sterically hindered

VO^{2+} : as a transient species

CN = 2 : rare, linear ($D_{\infty h}$)

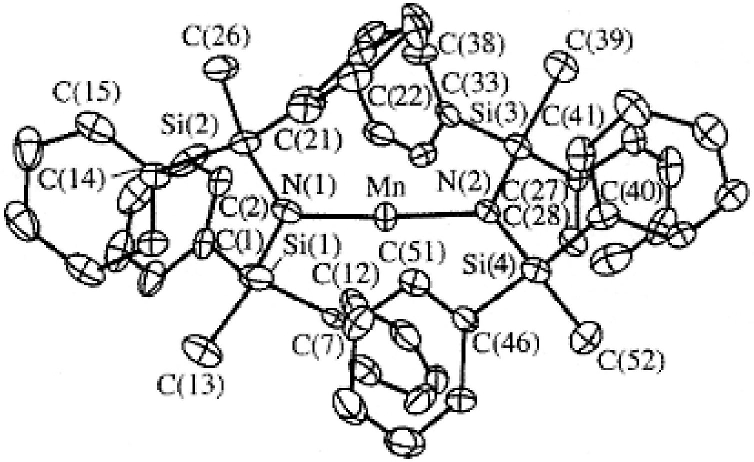
mostly d^{10} compounds

$[H_3N-Ag-NH_3]^+$

$[Cl-Cu-Cl]^-$

$NC-Hg-CN$

$[CN-Au-CN]^-$



$[Mn(N(SiMePh_2)_2)_2]$

None d^{10} complexes also exist.
ex) Mn(II) with bulky ligands

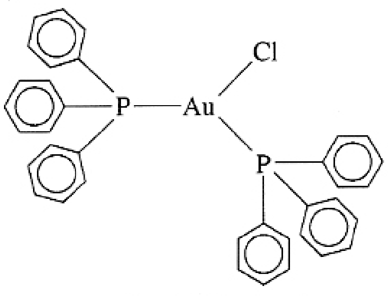
Coordination Numbers and Structures

CN = 1, 2, 3

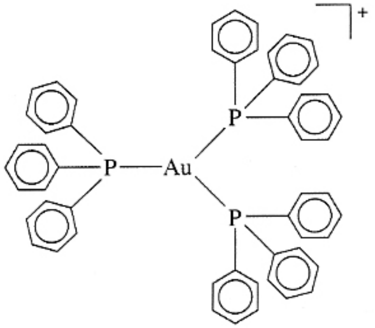
CN = 3 : rare, trigonal plane (D_{3h})

HgI_3^- (d^{10})

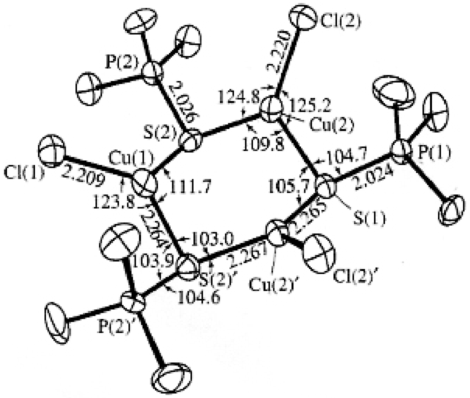
Complexes with bulky ligands



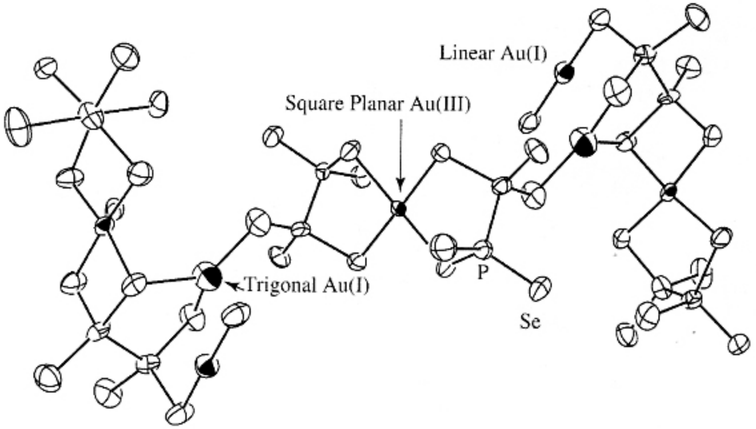
$[Au(PPh_3)_2Cl]$



$[Au(PPh_3)_3]^+$



$[Cu(SP(CH_3)_3Cl]_3$

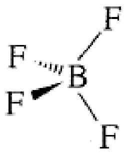


Coordination Numbers and Structures

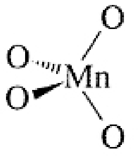
CN = 4

CN = 4 : tetrahedron (T_d), square plane (D_{4h})

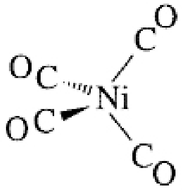
T_d: very common



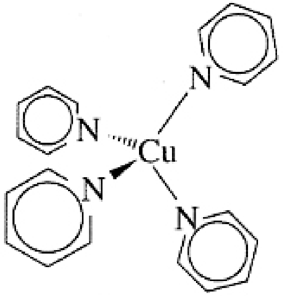
BF_4^-



MnO_4^-

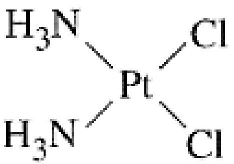


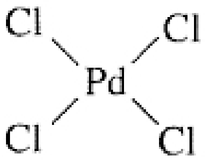
$Ni(CO)_4$



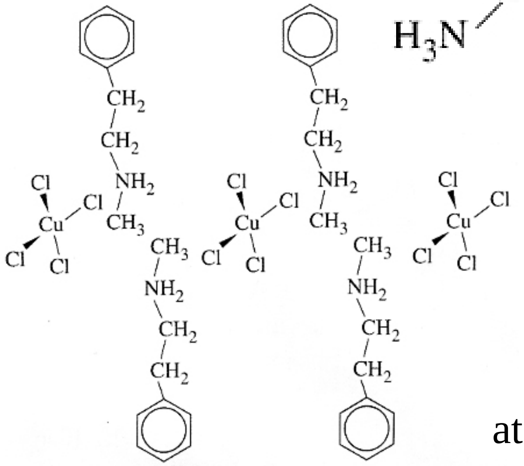
$[Cu(py)_4]^+$

D_{4h}: d^8 such as Ni(II), Pt(II), Pd(II)





and others



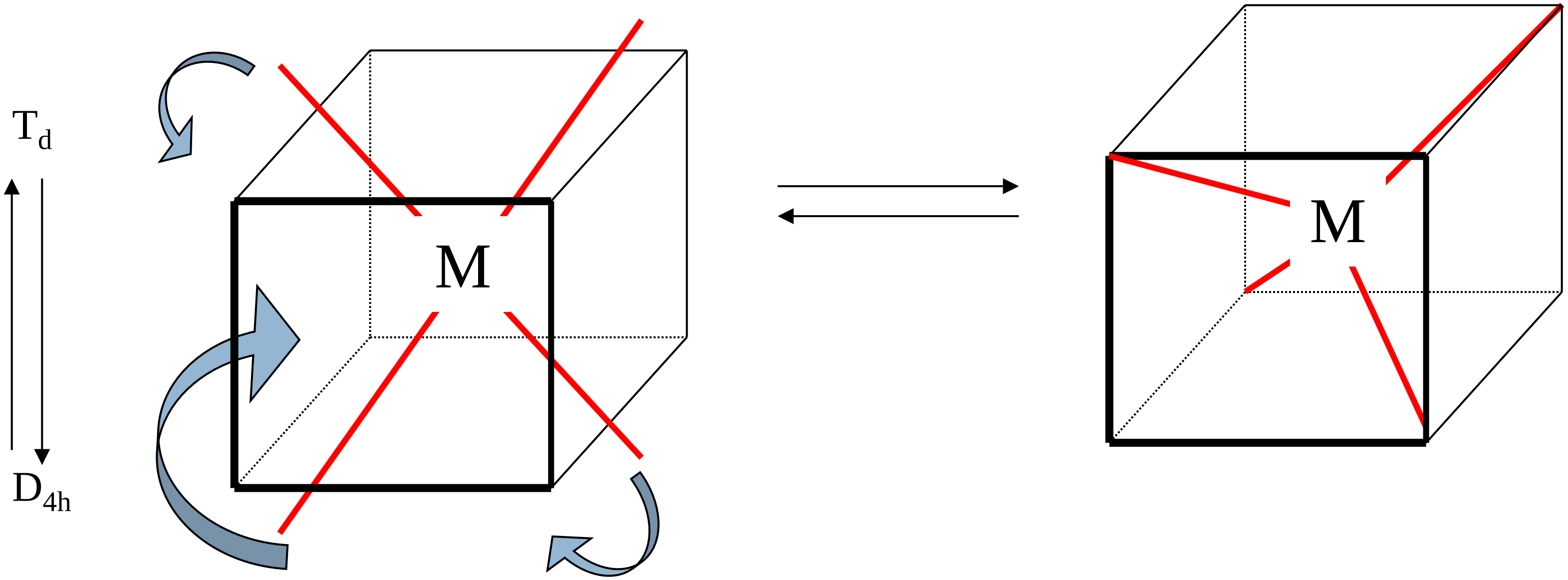
(T_d at 75°C)

at 25°C

Coordination Numbers and Structures

CN = 4

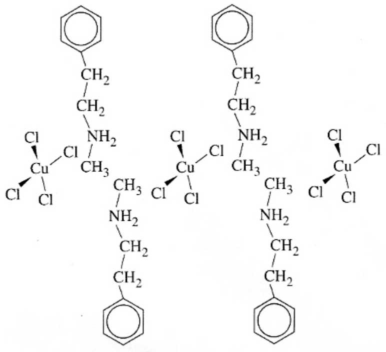
CN = 4 : tetrahedron (T_d), square plane (D_{4h})



ΔE is not big

$[NiBr_2(P(C_6H_5)_2(CH_2C_6H_5))_2]$: both T_d and D_{4h} in the same crystal

$[Ni(PR_3)_2X_2]$



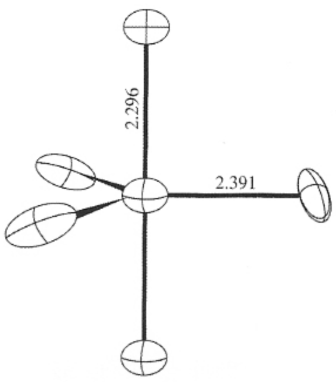
(T_d at 75°C)

at 25°C

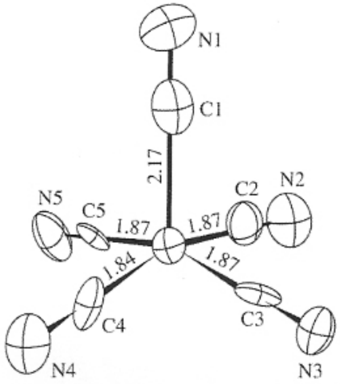
Coordination Numbers and Structures

CN = 5

CN = 5 : trigonal bipyramid (D_{3h}), square pyramid (C_{4v})

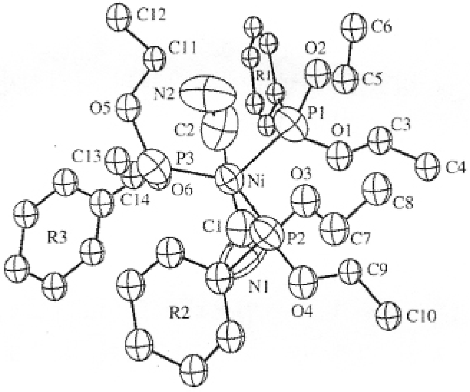


$[CuCl_5]^{3-}$



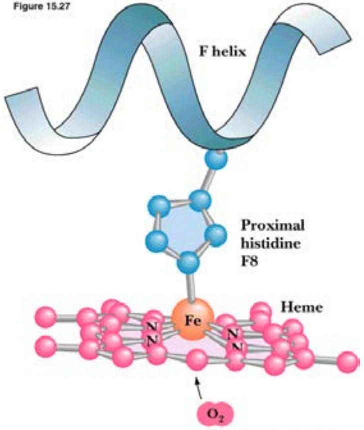
$[Ni(CN)_5]^{3-}$

D_{3h} and C_{4h} coexist in crystal

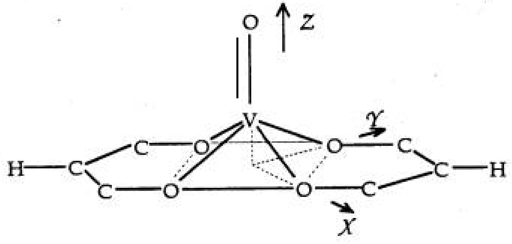


$[Ni(CN)_2(PPh(OEt)_2)_2]$

Garrett & Grisham: Biochemistry, 2/e
Figure 15.27

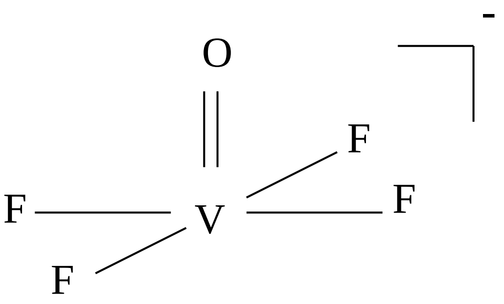


Saunders College Publishing



$VO(acac)_2$

V(IV): d^1

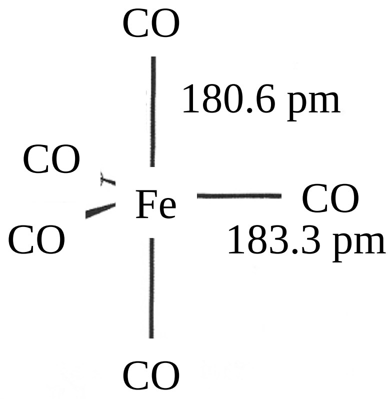


V(V):d^0

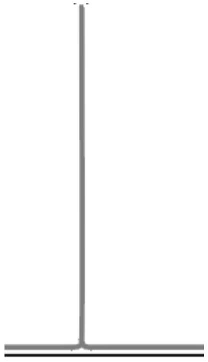
Coordination Numbers and Structures

CN = 5 : trigonal bipyramid (D_{3h}), square pyramid (C_{4v})

$Fe(CO)_5$



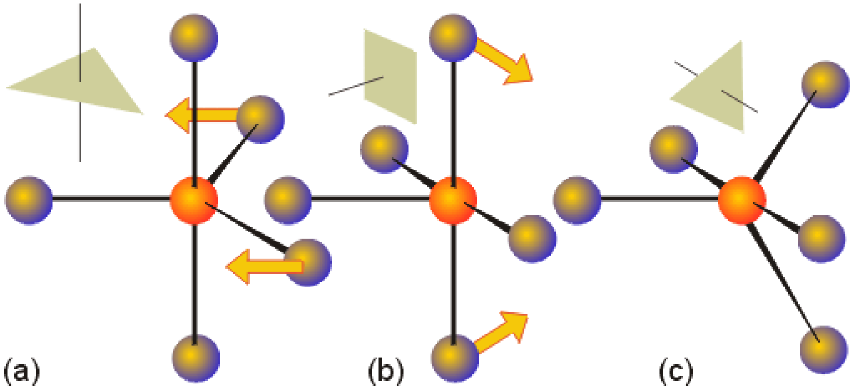
crystal



^{13}C NMR in solution

Fluxional behavior (Berry pseudorotation)

ΔE between D_{3h} and C_{4v} is very small.

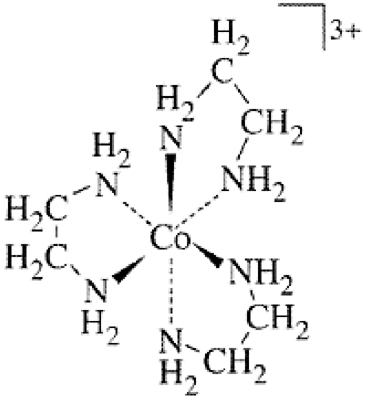


Coordination Numbers and Structures

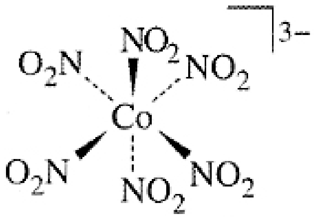
CN = 6

CN = 6 : octahedron (O_h)

octahedron (O_h): very common

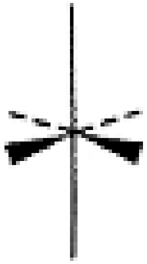


$[Co(en)_3]^{3+}$



$[Co(NO_2)_6]^{3-}$

variations of O_h

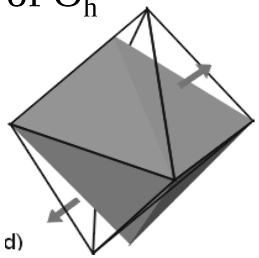


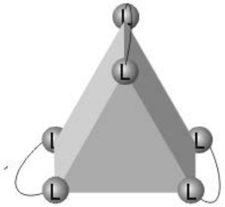
D_{4h}

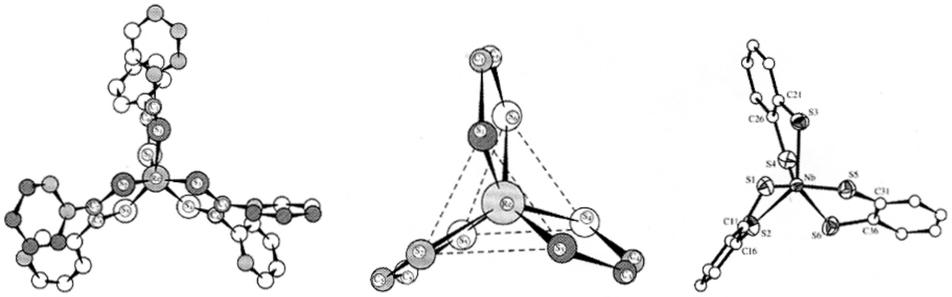
tetragonal elongation
ex) Cu(II) : d^9

tetragonal compression
ex) Ti(III) : d^1

variations of O_h







trigonal elongation
: trigonal antiprism (D_{3d})

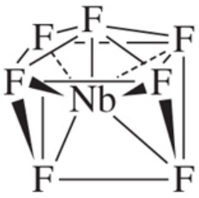
and 60° rotation
: trigonal prism (D_{3h})

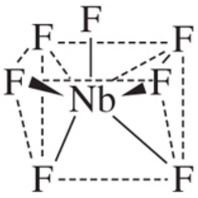
usually with three bidentate ligands

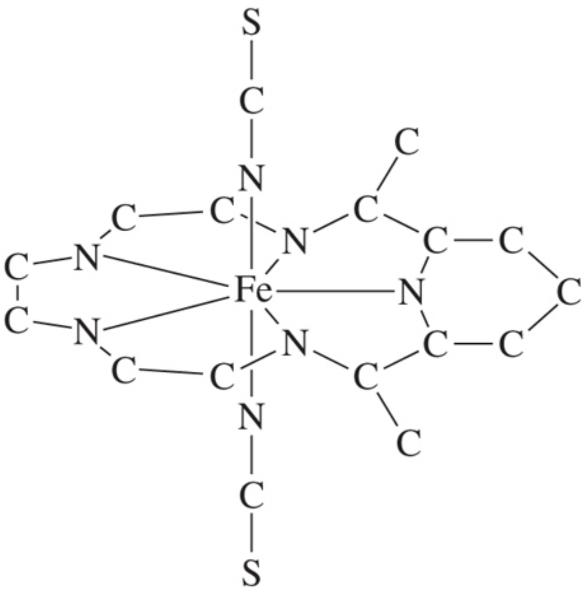
Coordination Numbers and Structures

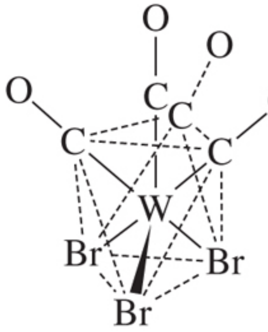
CN = 7

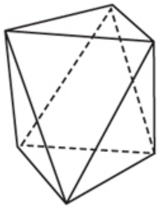
CN = 7 : pentagonal bipyramid (D_{5h})
capped trigonal prism, capped octahedron





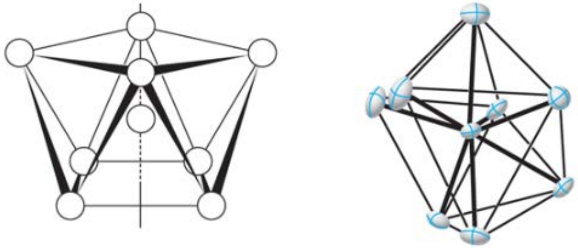




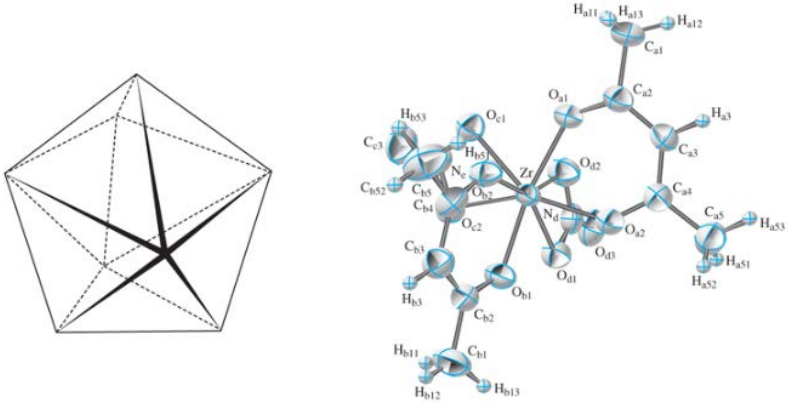


Coordination Numbers and Structures

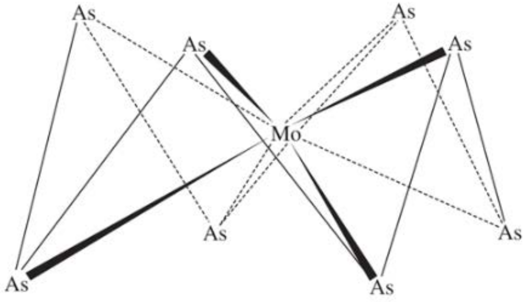
CN ≥ 8



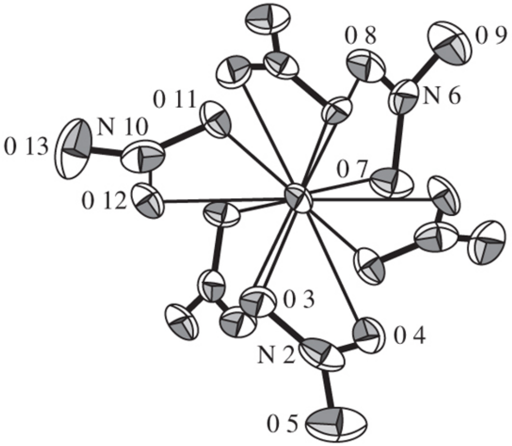
(a)

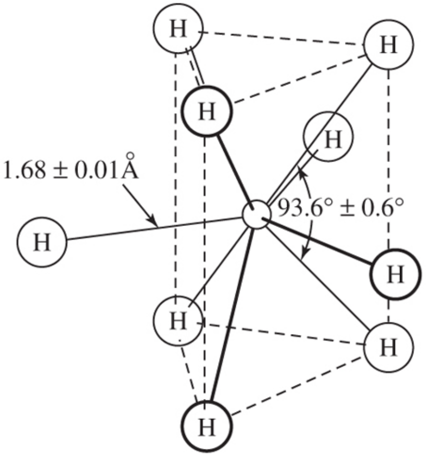


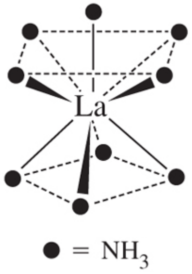
(b)



(c)



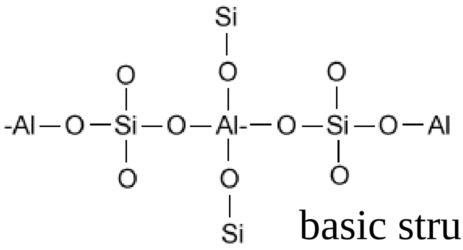




Coordination Frameworks

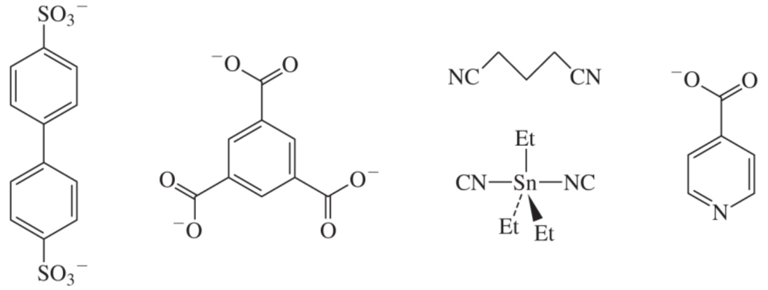
Ligand can act as bridges to create more extended structures.

Zeolites are microporous, aluminosilicate, minerals commonly used as commertial adsorbents.

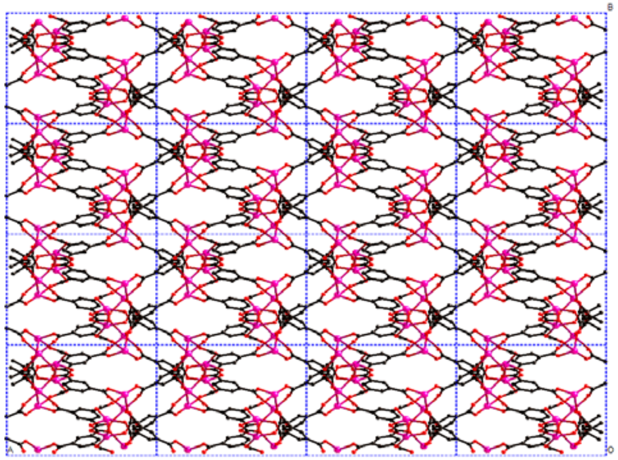


basic structure

Metal-Organic Frameworks **(MOF**s**)** are crystalline compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one-, two-, or three-dimensional structures that can be porous.



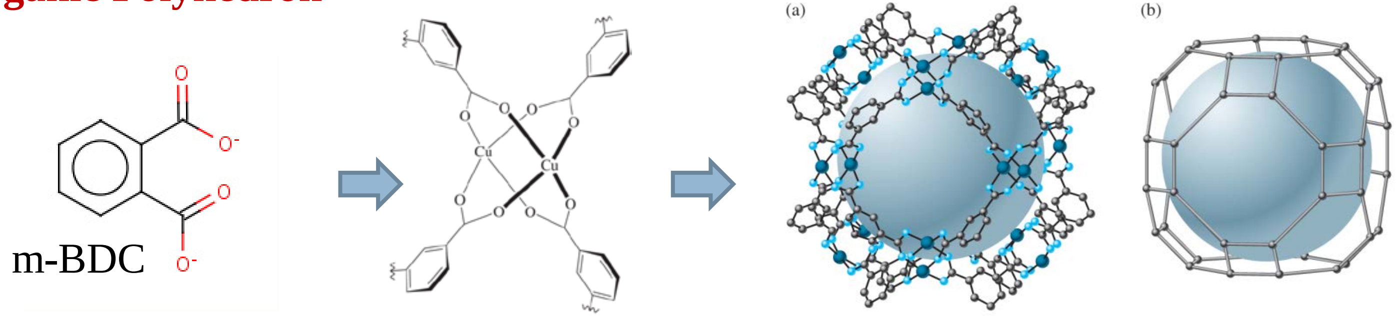
ligand “building block”



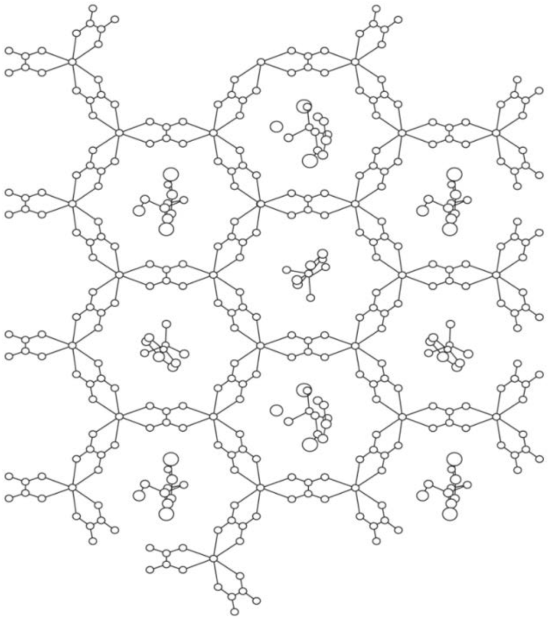
MOF

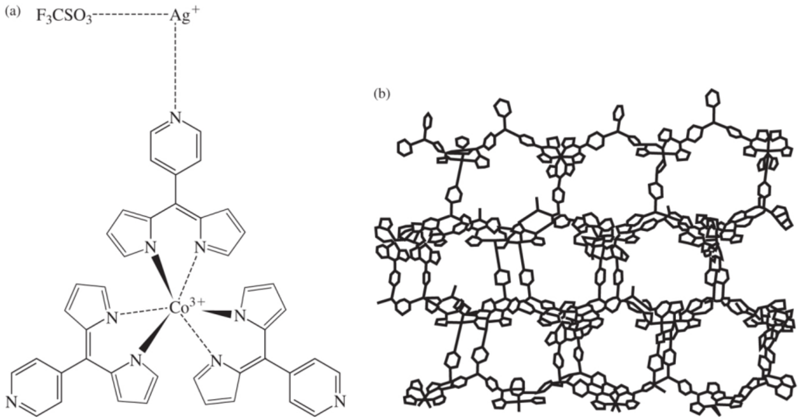
Coordination Frameworks

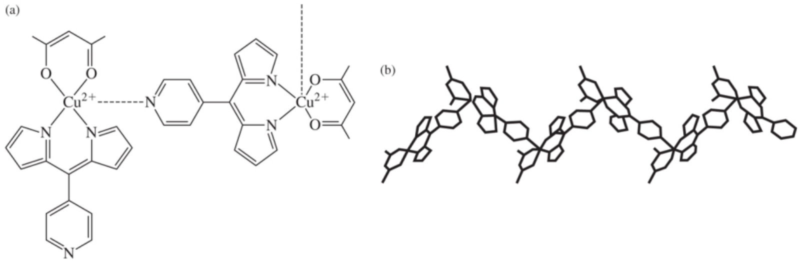
Metal-Organic Polyhedron



Many other MOFs



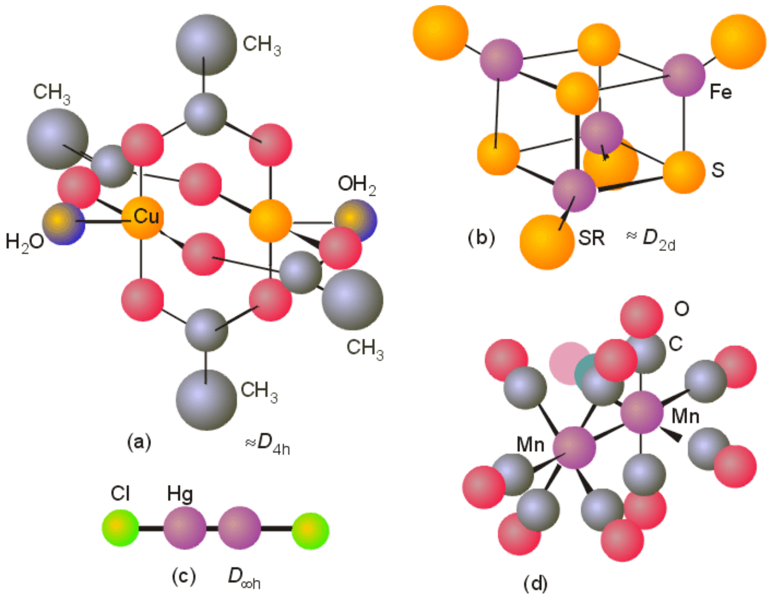


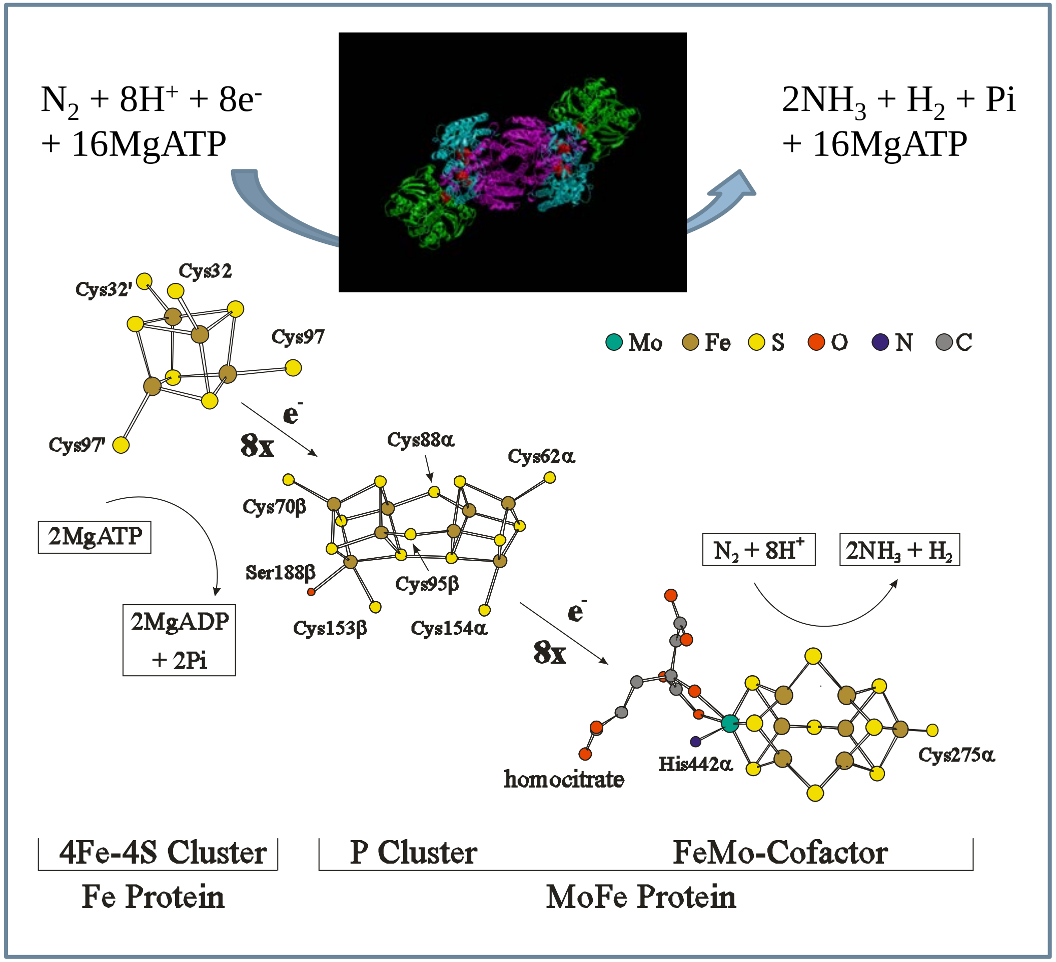


Multimetallic Complexes

metal clusters: with direct M-M bonds (in real world, metal cluster is more common for both)

cage complexes: without direct M-M bonds





$N_2 + 8H^+ + 8e^-$
$+ 16MgATP$

$2NH_3 + H_2 + Pi$
$+ 16MgATP$

$N_2 + 8H^+$ → $2NH_3 + H_2$

4Fe-4S Cluster — Fe Protein

P Cluster, FeMo-Cofactor — MoFe Protein

Metal-sulfur clusters in Nitrogenase