Chapter 9 Coordination Chemistry I: Structure and Isomers

9-1 History
9-2 Nomenclature
9-3 Isomerism
9-4 Coordination Numbers and Structure

History

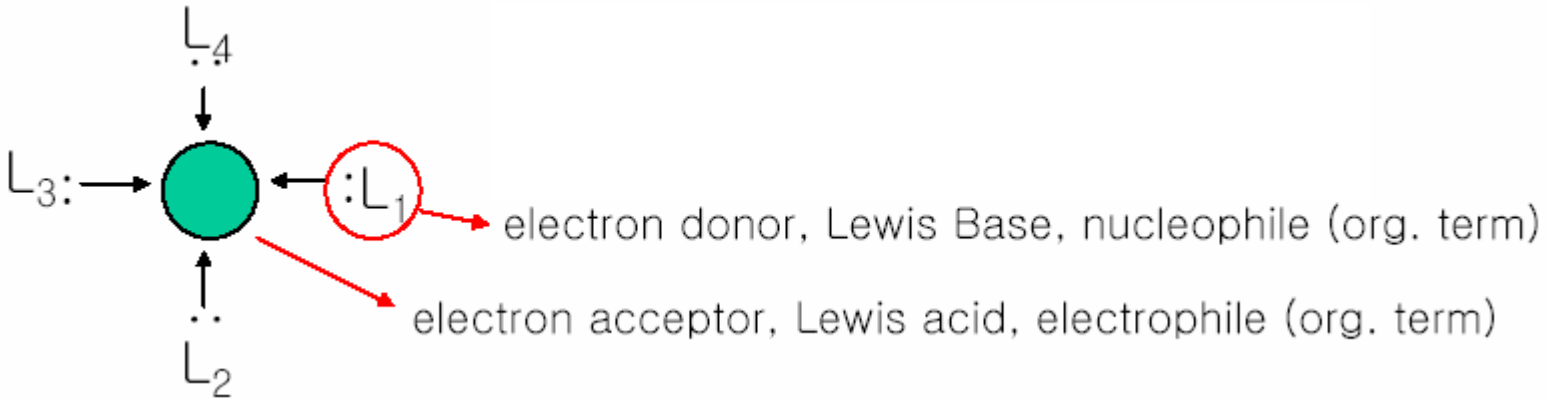
What is coordination compound?

Coordniantion compounds include compound composed of a **metal atom or ion** and **one or more ligands** that formally donate electrons to the metal.

More specifically, a transition metal sorrounded by neutral molecules or anions with a definite geometry.

What is ligand?

Ligand can be a **atom, ion, and molecules**.



History

Prussian blue (German: *Preußischblau* or *Berliner Blau*, in English **Berlin blue**) is a dark blue pigment used in paints and formerly in blueprints. Prussian blue was discovered by accident by painter Heinrich Diesbach in Berlin in 1704-5, which is why it is also known as Berlin blue. (Diesbach was attempting to create a paint with a red hue.) It has several different chemical names, these being iron(III) ferrocyanide, ferric ferrocyanide, iron(III) hexacyanoferrate(II), and ferric hexacyanoferrate. Commonly and conveniently it is simply called "PB.

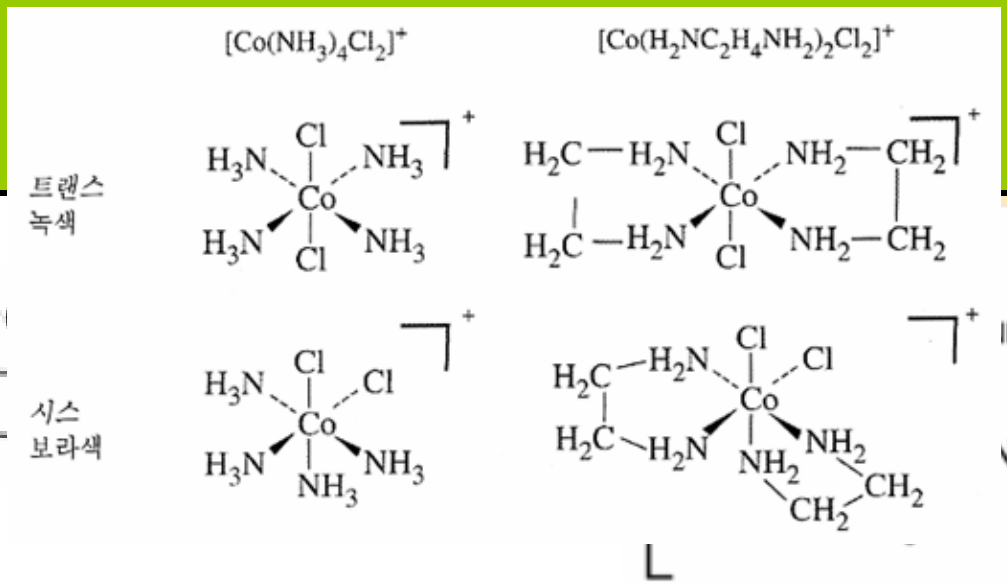
Aureolin (sometimes called **Cobalt Yellow**) is a pigment used in oil and watercolor painting. Its color index name is PY40 (40th entry on list of yellow pigments). It was first made in 1851 and its chemical composition is potassium cobaltinitrite.

Copper(II) sulfate ("sulphate" in most Commonwealth nations) is the chemical compound with the formula $CuSO_4$. This salt exists as a series of compounds that differ in their degree of hydration. The anhydrous form is a pale green or gray-white powder, while the pentahydrate, the most commonly encountered salt, is bright blue. This hydrated copper sulfate occurs in nature as the mineral called chalcanthite. The archaic name for copper(II) sulfate is "blue vitriol" or "bluestone"

Alfred Werner

Nobel Prize for Chemistry
1913

For complexes with more than one type of ligand, Werner succeeded in explaining the number of isomers observed. For exemple, he explained the existence of two isomers of "$Co(NH_3)_4Cl_3$", one green and one purple. Werner proposed that these are two geometric isomers of formula $[Co(NH_3)_4Cl_2]Cl$, with one Cl^- ion dissociated as confirmed by conductivity measurements. The Co atom is surrounded by four NH_3 and two Cl ligands at the vertices of an octahedron. The green isomer is "trans" with the two Cl ligands at opposite vertices, and the purple is "cis" with the two Cl at adjacent vertices.



History

What is coordination compound?

Coordination complexes were known - although not understood in any sense - since the beginning of chemistry, e.g. Prussian blue, Aureolin, and copper vitriol.

The key breakthrough occurred when Alfred Werner proposed, *inter alia*, that Co(III) bears six ligands in an octahedral geometry.

The theory allows one to understand the difference between coordinated and ionic chloride in the cobalt ammine chlorides and to explain many of the previously inexplicable isomers.

He resolved the first coordination complex into optical isomers, overthrowing the theory that chirality was necessarily associated with carbon compounds.

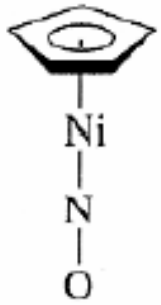
History

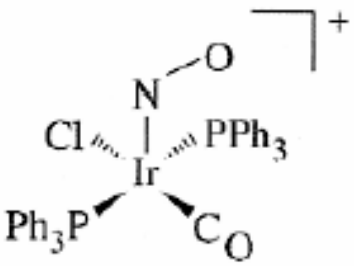
What is ligand?

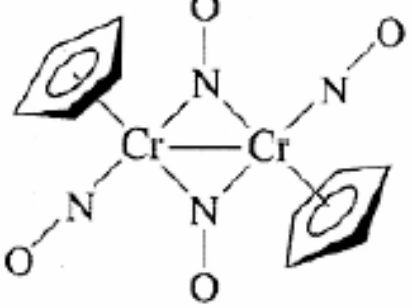
In chemistry, a **ligand** is an atom, ion, or molecule that generally donates one or more of its electrons through a coordinate covalent bond to one or more central atoms or ions (these ligands act as a Lewis base).

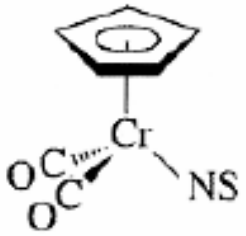
The ligands that are directly bonded to the metal (that is, share electrons), are called "**inner sphere**" ligands.
If the inner-sphere ligands do not balance the charge of the central atom, this may be done by simple ionic bonding with another set of counter ions (the "**outer-sphere**" ligands).
The complex of the metal with the inner sphere ligands is then called a complex ion (which can be either cationic or anionic).
The complex, along with its counter ions, is called a coordination compound. The size of a ligand is indicated by its cone angle.

History









Organometallic chemistry is the study of chemical compounds containing **bonds between carbon and a metal**.

Organometallic chemistry combines aspects of inorganic chemistry and organic chemistry.

Organometallic compounds find practical use in stoichiometric and catalytically active compounds.

Electron counting is key in understanding organometallic chemistry. The 18-electron rule is helpful in predicting the stabilities of organometallic compounds. Organometallic compounds which have 18 electrons (filled s, p, and d orbitals) are relatively stable. This suggests the compound is isolable, but it can result in the compound being inert.

Nomenclature
– Common Monodentate Ligands

Ambidentate Ligand

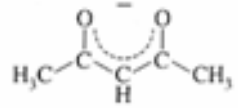
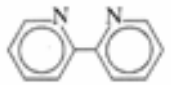
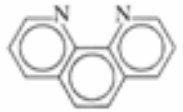
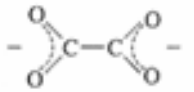
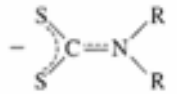
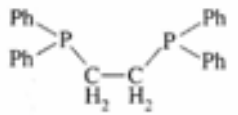
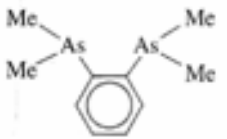
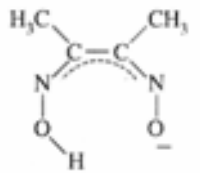
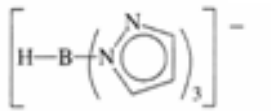
관용명	IUPAC 명칭	화학식
플루오로(fluoro)	플루오로(fluoro)	F^-
클로로(chloro)	클로로(chloro)	Cl^-
브로모(bromo)	브로모(bromo)	Br^-
아이오도(iodo)	아이오도(iodo)	I^-
아지도(azido)	아지도(azido)	N_3^-
사이아노(cyano)	사이아노(cyano)	CN^-
싸이오사이아노(thiocyano)	싸이오사이아네이토-S (S-결합)	SCN^-
아이소싸이오사이아노(isothiocyano)	싸이오사이아네이토-N (N-결합)	NCS^-
하이드록소(hydroxo)	하이드록소(hydroxo)	OH^-
아쿠아(aqua)	아쿠아(aqua)	H_2O
카보닐(carbonyl)	카보닐(carbonyl)	CO
싸이오카보닐(thiocarbonyl)	싸이오카보닐(thiocarbonyl)	CS
나이트로실(nitrosyl)	나이트로실(nitrosyl)	NO^+
나이트로(nitro)	나이트로-N (N-결합)	NO_2^-
나이트라이토(nitrito)	나이트라이토-O (O-결합)	ONO^-
메틸 아이소사이아나이드 (methyl isocyanide)	메틸아이소사이아네이트 (methylisocyanate)	CH_3CN
포스핀(phosphine)	포스페인(phosphane)	PR_3
피리딘(pyridine)	피리딘(pyridine)	py
암민(ammine)	암민(ammine)	NH_3
메틸아민(methylamine)	메틸아민(methylamine)	$MeNH_2$
아미도(amido)	아미도(amido)	NH_2^-

Nomenclature
– Common Chelating Amines

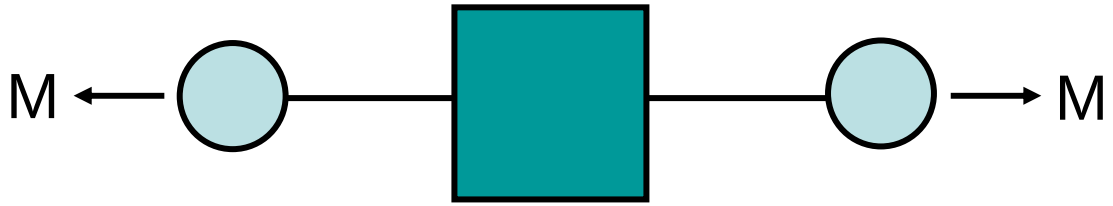
자리수	관용명	IUPAC 명칭	약식어	화학식
한 자리	암민, 메틸아민	암민, 메틸아민		NH_3, CH_3NH_2
두 자리	에틸렌다이아민	1,2-에테인다이아민	en	$NH_2CH_2CH_2NH_2$
세 자리	다이에틸렌트라이아민	2,2′-다이아미노다이에틸아민 또는 1,4,7-트라이아자헵테인	dien	$NH_2CH_2CH_2NHCH_2CH_2NH_2$
네 자리	트라이에틸렌테트라아민	1,4,7,10-테트라아자데케인	trien	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
	β, β′, β″-트라이아미노 트라이에틸아민	β, β′, β″-트리스(2-아미노 에틸)아민	tren	$NH_2CH_2CH_2N(CH_2CH_2NH_2)CH_2CH_2NH_2$
다섯 자리	테트라 에틸렌펜타아민	1,4,7,10,13-펜타아자 트라이데케인		$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
여섯 자리	에틸렌다이아민 테트라아세테이트	1,2-에테인다이일(다이나이트릴로)테트라아세테이트	EDTA	$^-OOCCH_2$, CH_2COO^-, NCH_2CH_2N, $^-OOCCH_2$, CH_2COO^-

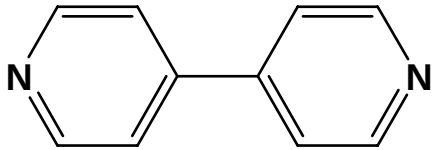
Monodentate, bidentate, tri-, tetra-, penta-, hexadentate

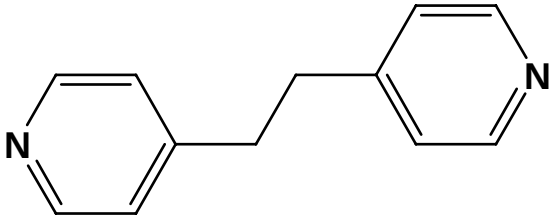
Nomenclature
– Common Multidentate (chelating) Ligands

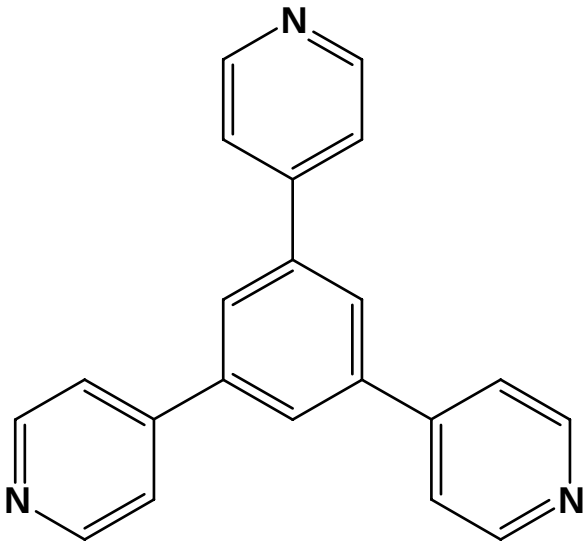
관용명	IUPAC 명칭	약식어	화학식과 구조	
아세틸아세토네이토	2,4-펜테인다이오노	acac	$CH_3COCHCOCH_3^-$	
2,2′-바이피리딘	2,2′-바이피리딜	bipy	$C_{10}H_8N_2$	
1,10-페난트롤린 또는 페난트롤린	1,10-다이아미노페난트렌	phen, *o*-phen	$C_{12}H_8N_2$	
옥살레이토	옥살레이토	ox	$C_2O_4^{2-}$	
다이알킬 다이싸이오카바메이토	다이알킬 카바모다이싸이오에이토	dtc	$S_2CNR_2^-$	
1,2-비스(다이페닐 포스피노)에테인	1,2-에테인다이일비스 (다이페닐포스페인)	dppe	$Ph_2PC_2H_4PPh_2$	
o-페닐렌비스 (다이메틸아르신)	1,2-페닐렌비스 (다이메틸아르세인)	diars	$C_6H_4(As(CH_3)_2)_2$	
다이메틸글리옥시메이토	뷰테인다이엔 다이옥심	DMG	$HONCC(CH_3)C(CH_3)NO^-$	
피라졸릴보레이토	하이드로트리스- (피라조-1-일)보레이토			

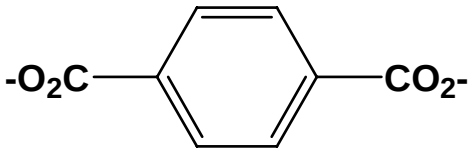
Nomenclature
– Bridging Ligands

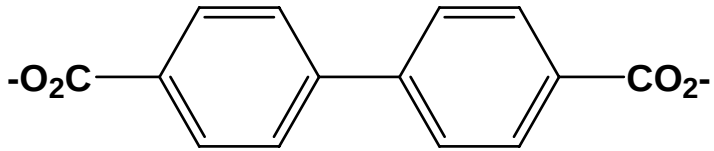






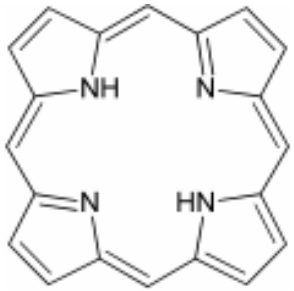




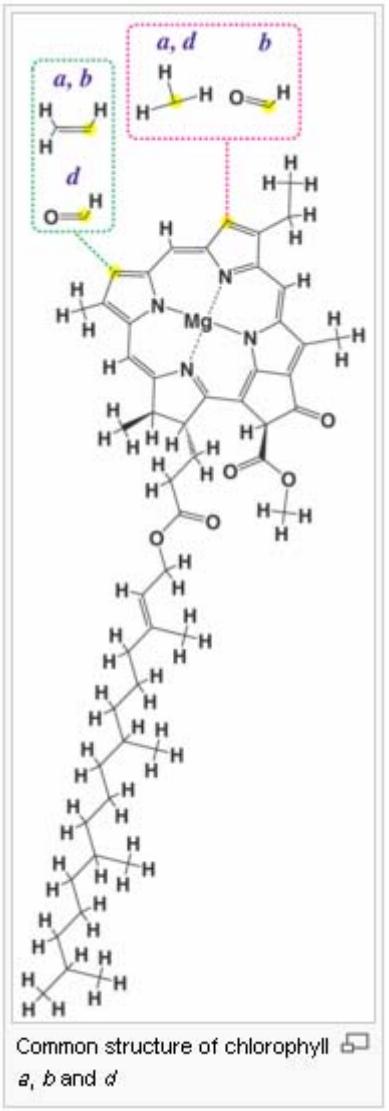


Nomenclature
– Modern Ligands (Porphyrin)

Porphyrin



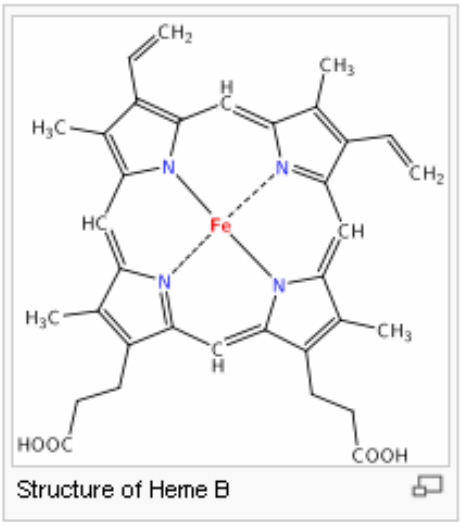
Porphyrin coordinated to magnesium: chlorophyll



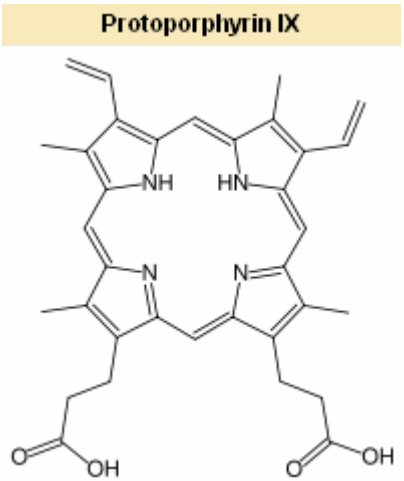
Common structure of chlorophyll *a*, *b* and *d*

Photodynamic Therapy(PDT)

Porphyrin coordinated to iron: heme

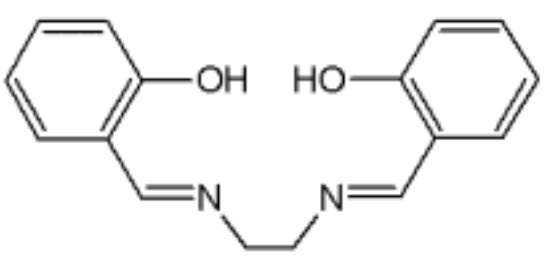


Structure of Heme B

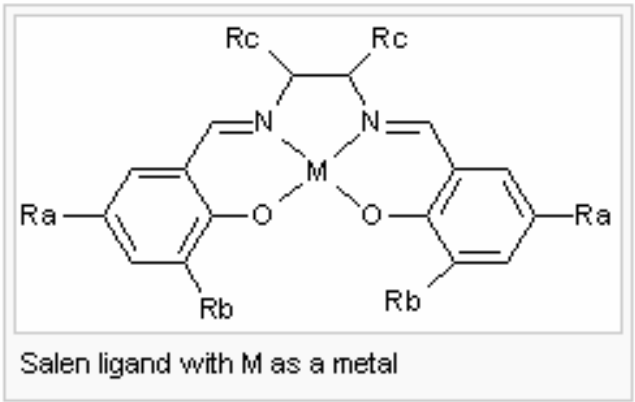


Nomenclature
– Modern Ligands

Salen

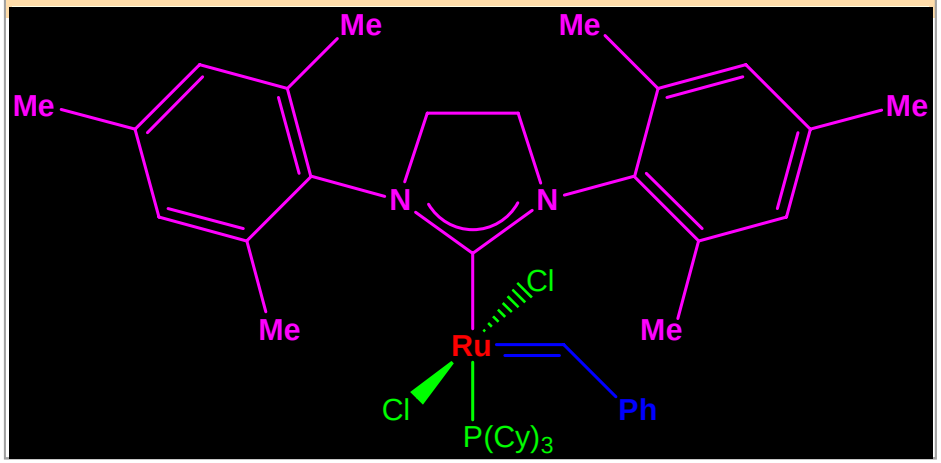


Jacobsen epoxidation



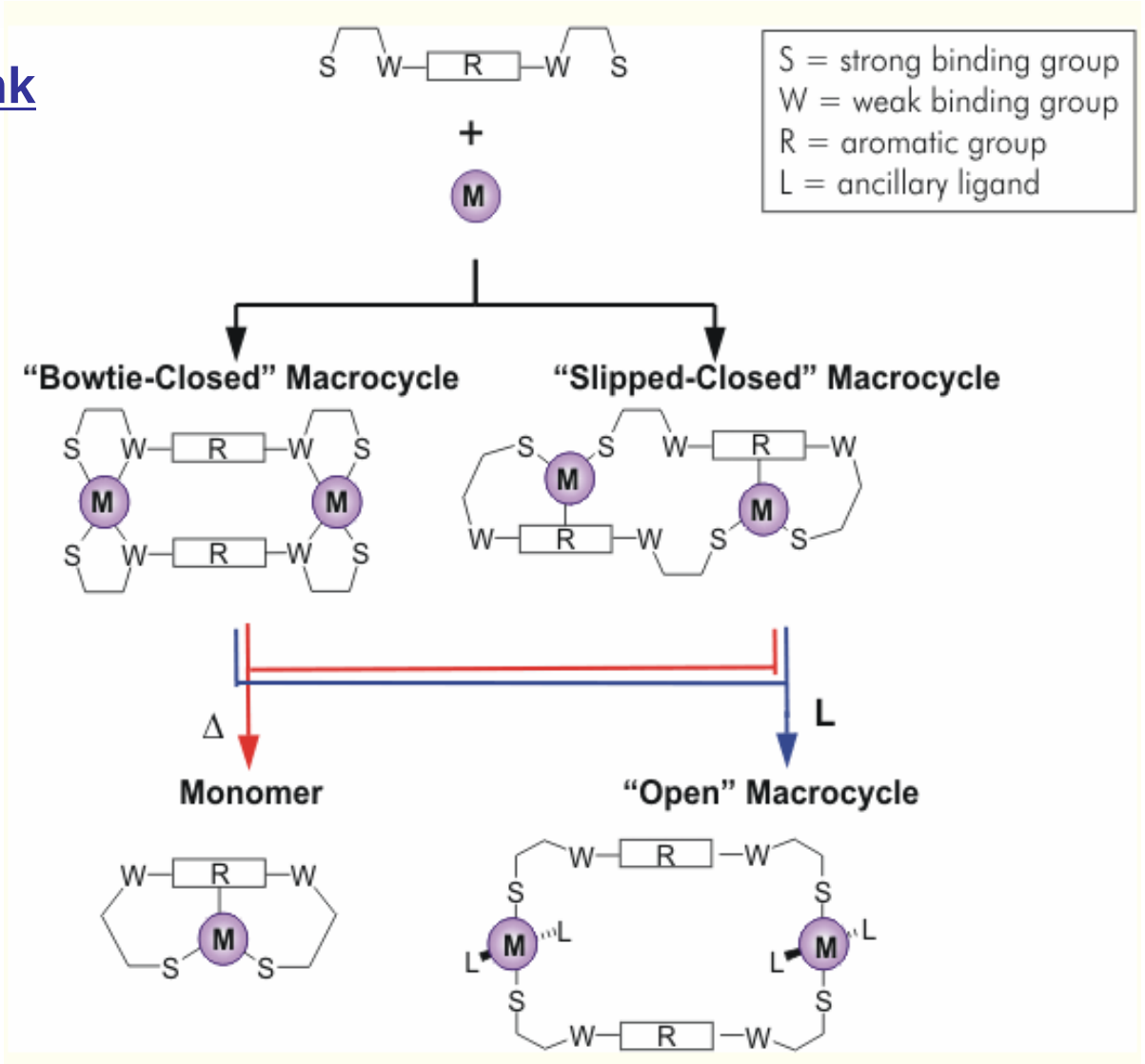
Salen ligand with M as a metal

Grubbs' Catalyst 2nd Generation



Nomenclature
– Modern Ligands (Weak-Link Approach)

Mirkin's Weak-Link



Nomenclature
– Nomenclature Rules

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			

1. Cation comes first, followed by anion

$[Ag(NH_3)_2]Cl$: diamminesilver(I) chloride
$K_3[Fe(CN)_6]$: potassium hexacyanoferrate(III)

2. The inner coordination sphere is enclosed in square brackets in the formula.
   Nomenclature: Ligand → Metal
   Formula: Metal → Ligand

$[Cu(NH_3)_4]SO_4$: tetraamminecopper(II) sulfate
$[Co(NH_3)_6]Cl_3$: hexaamminecobalt(II) chloride

3. Prefixe

$[Co(en)_2Cl_2]^+$: dichlorobis(ethylenediamine)cobalt(II)
$[Fe(bipy)_3]^{2+}$: tris(bipyridine)iron(II)

Nomenclature
– Nomenclature Rules

4. Ligands are named in alphabetical order. (not prefix)

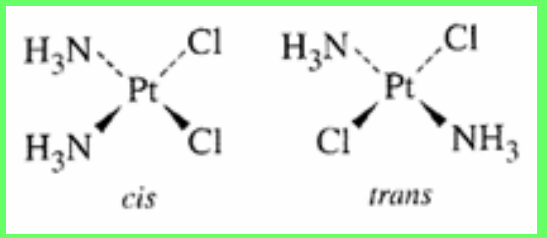
$[Co(NH_3)_4Cl_2]^+$: tetraamminedichlorocobalt(III)
$Pt(NH_3)BrCl(CH_3NH_2)$: amminebromochloromethylamineplatinum(II)

5. Anionic ligands are given an **o** suffix.
   Neutral ligands retain their name.
   Water is called aqua.
   Ammonia is called amine.
6. Designating charge or oxidation number
   Stock system: oxidation number of the metal as a Roman nummeral in parentheses.
   Ewing-Bassett system: charge on the coordination sphere in parentheses

$[Pt(NH_3)_4]^{2+}$: tetraammineplatinum(II) tetraammineplatinum(2+)
$[PtCl_4]^{2-}$: tetrachloroplatinate(II) tetrachloroplatinate(2-)
$[PtCl_6]^{2-}$: hexachloroplatinate(IV) hexachloroplatinate(2-)

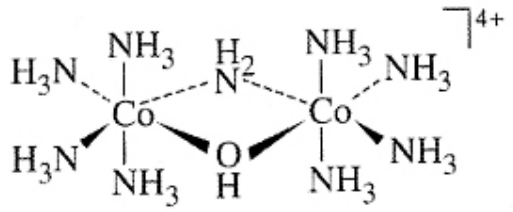
Nomenclature
– Nomenclature Rules

7. The prefixs cis- and trans- designate adjacent and opposite



8. Bridging ligands between metal ions have the prefix μ.

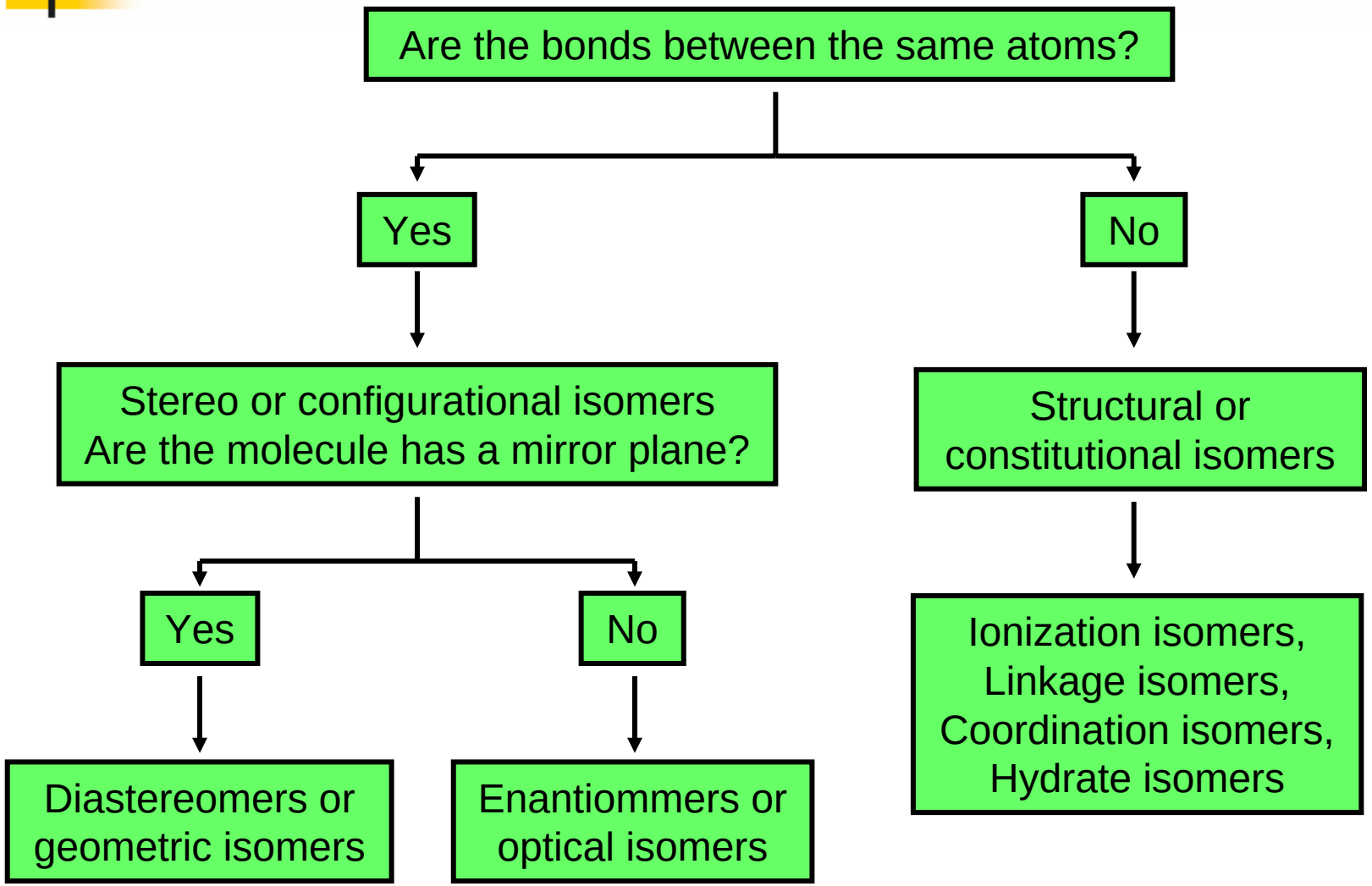
그림 9-6 아마이드와 하이드록소 리간드가 다리 리간드로 결합되어 있는 μ-아미도-μ-하이드록소 비스(테트라암민코발트)(4 +) (μ-amido-μ-hydroxobis(tetraamminecobalt) (4 +)), $[(NH_3)_4Co(OH)(NH_2)Co(NH_3)_4]^{4+}$.



9. When the complexs is negatively chared.

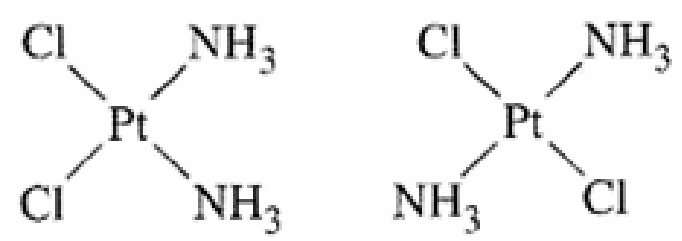
special names: iron(Fe) ferrate
silver(Ag) argentate
gold(Au) aurate
lead(Pb) plumate
tin(Sn) stannate

Isomerism

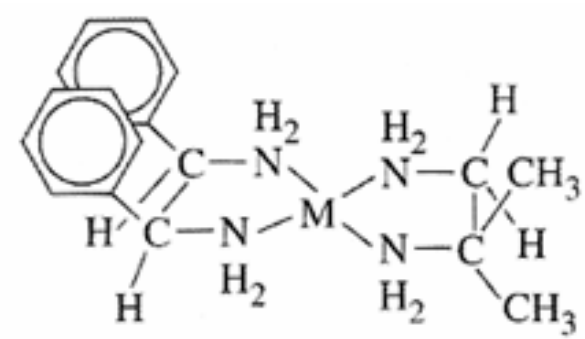

Are the bonds between the same atoms?
Yes
No
Stereo or configurational isomers
Are the molecule has a mirror plane?
Structural or constitutional isomers
Yes
No
Ionization isomers, Linkage isomers, Coordination isomers, Hydrate isomers
Diastereomers or geometric isomers
Enantiommers or optical isomers

Isomerism - Stereoisomers

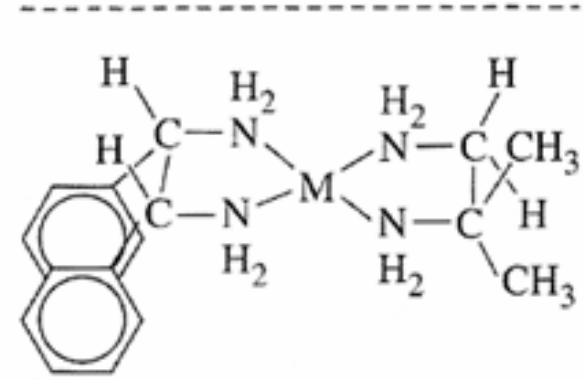
4 CN ; Square planar



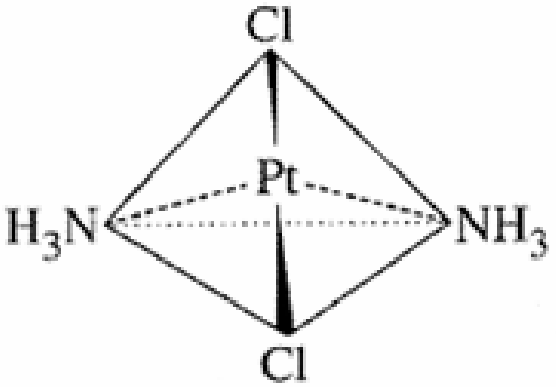
Cis and trans



Chiral isomers

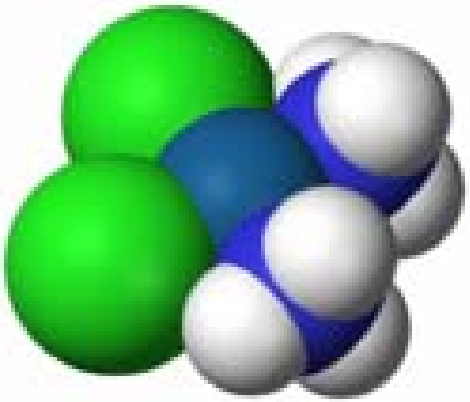


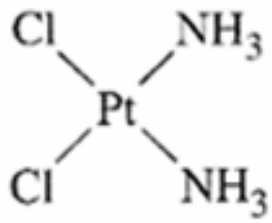
4 CN ; Tetrahedral
Only one structure



Isomerism - Stereoisomers

4 CN ; Square planar



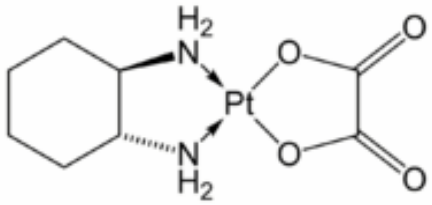


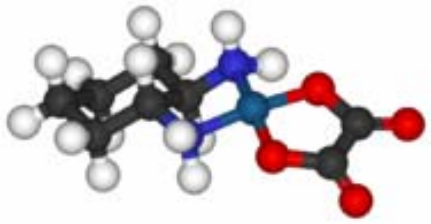
Cis and

Cisplatin, **cisplatinum** or **cis-diamminedichloroplatinum(II) (CDDP)** is a platinum-based chemotherapy drug used to treat various types of cancers,
It was the first member of its class, which now also includes carboplatin and oxaliplatin.

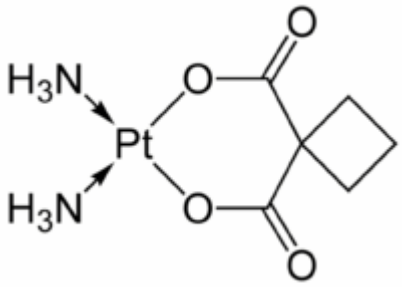
Antitumor agent: cisplatin

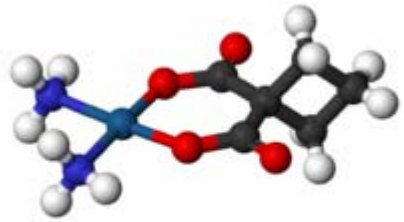
Chelate can induce the cis structure





Oxaliplatin

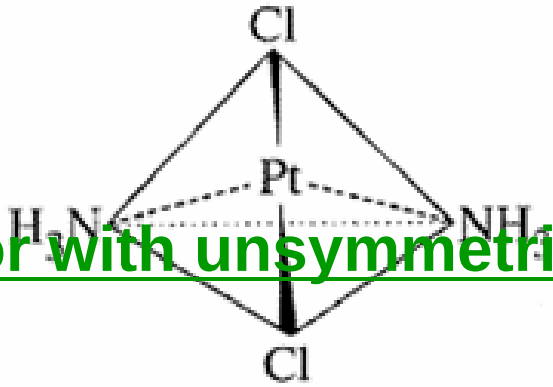




Carboplatin

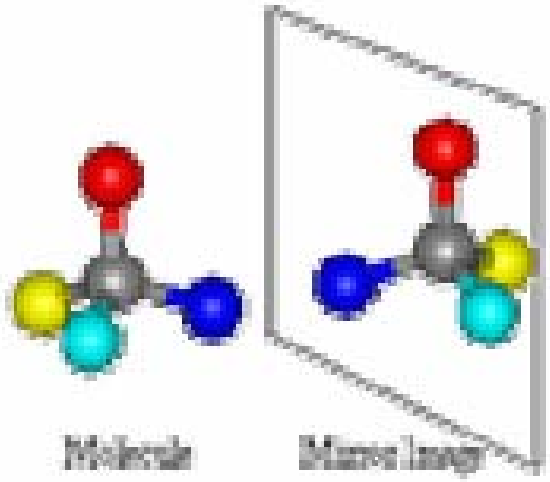
Isomerism - Stereoisomers

4 CN ; Tetrahedral
Only one structure



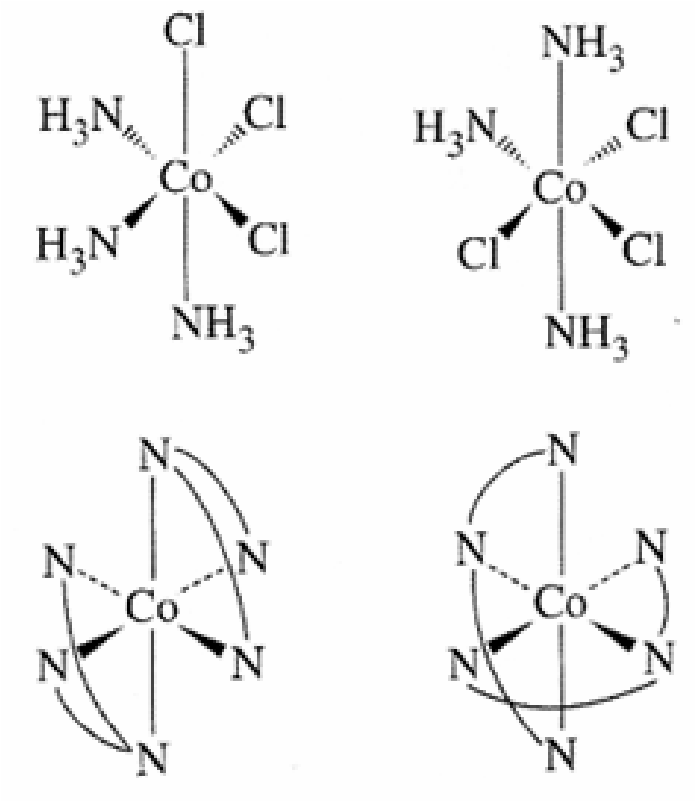
With four different ligands or with unsymmetrical chelating ligands

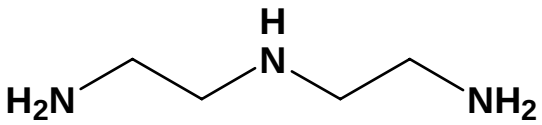
Three?



Isomerism - Stereoisomers

6 CN ; Octahedron



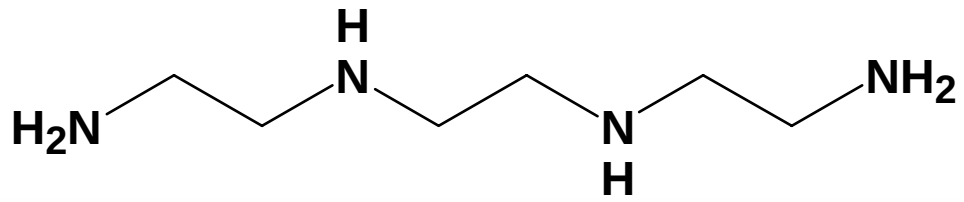


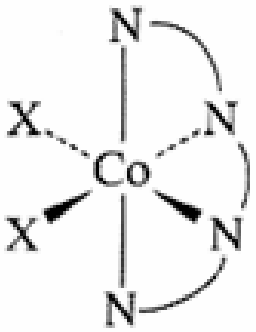
diethylenetriamine

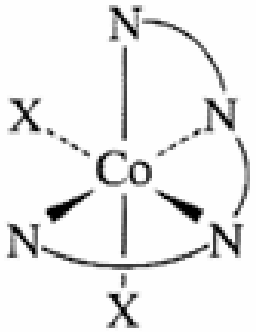
facial and meridional

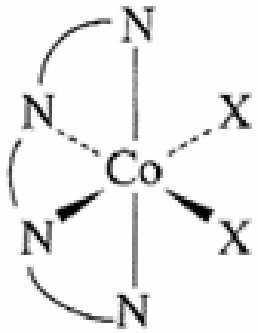
Isomerism - Stereoisomers

6 CN ; Octahedron, Triethylentetraamine

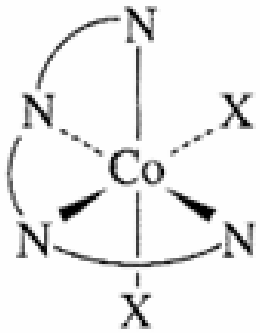




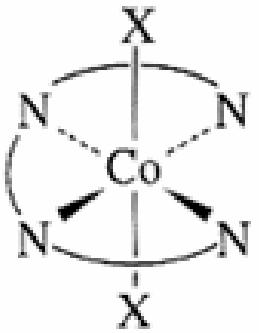




α



β



trans

Isomerism - Stereoisomers

Number of possible Isomers

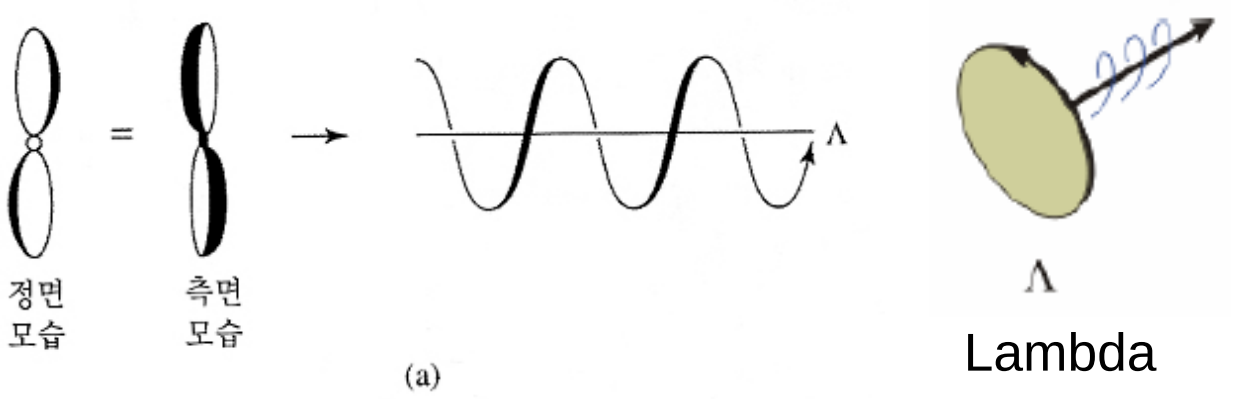
표 9-6
특정한 착화합물들의 이성질체수와 거울상 이성질체쌍의 수

화학식	입체 이성질체의 수	카이랄 이성질체쌍의 수
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

주: 대문자로 표기된 리간드는 킬레이트 리간드이고, 소문자로 표기된 것은 한 자리 리간드이다.

Isomerism – Stereoisomers: Combination of Chelate Rings (Λ, Δ)

Handedness of chelate Rings



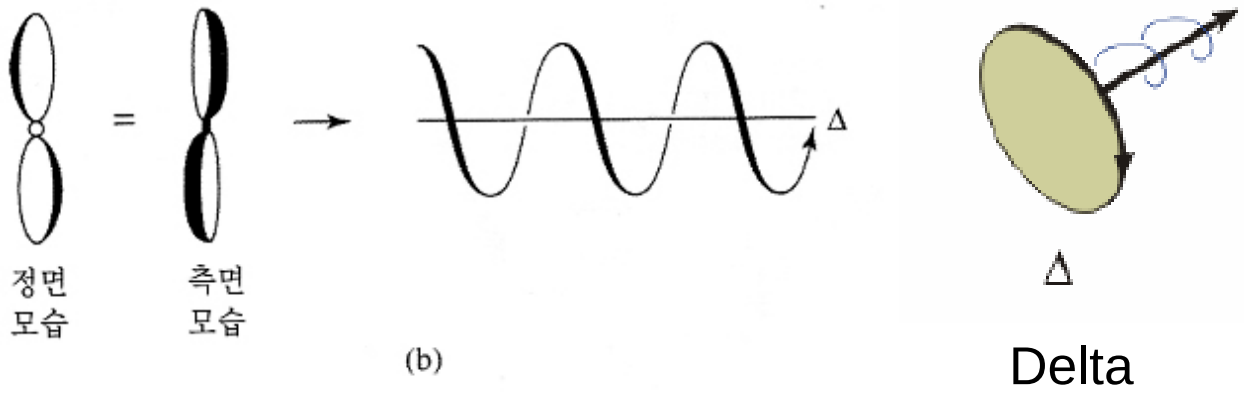


그림 9-12 오른쪽손과 왼쪽손 성질을 가지는 프로펠러들. (a) 왼손성(left-handed) 프로펠러와 날 끝부분의 궤적에 의해 만들어진 나선 모양. (b) 오른손성(right-handed) 프로펠러와 날 끝부분의 궤적에 의해 만들어진 나선 모양.

Isomerism – Stereoisomers: Combination of Chelate Rings (∧, Δ)

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

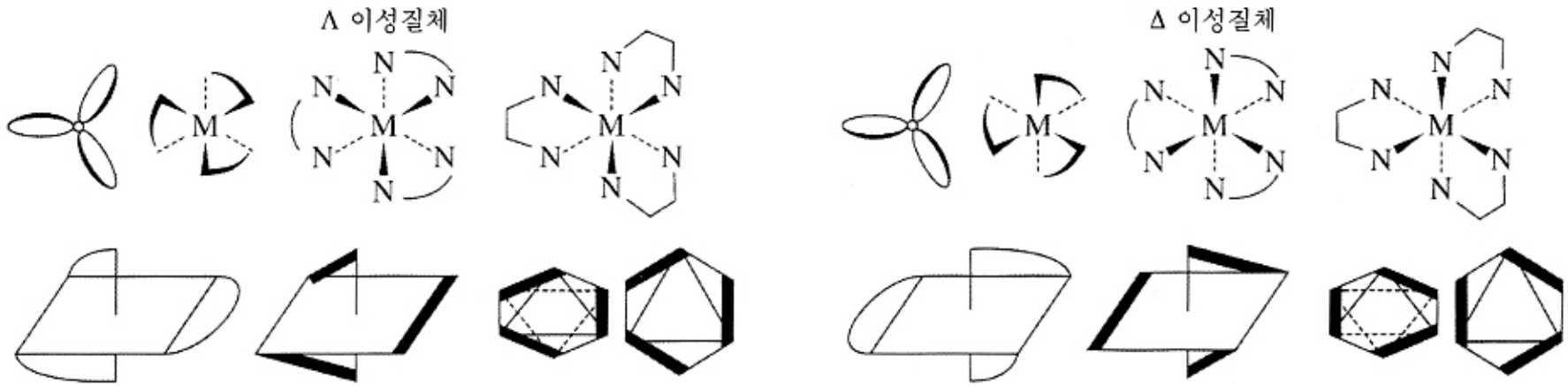


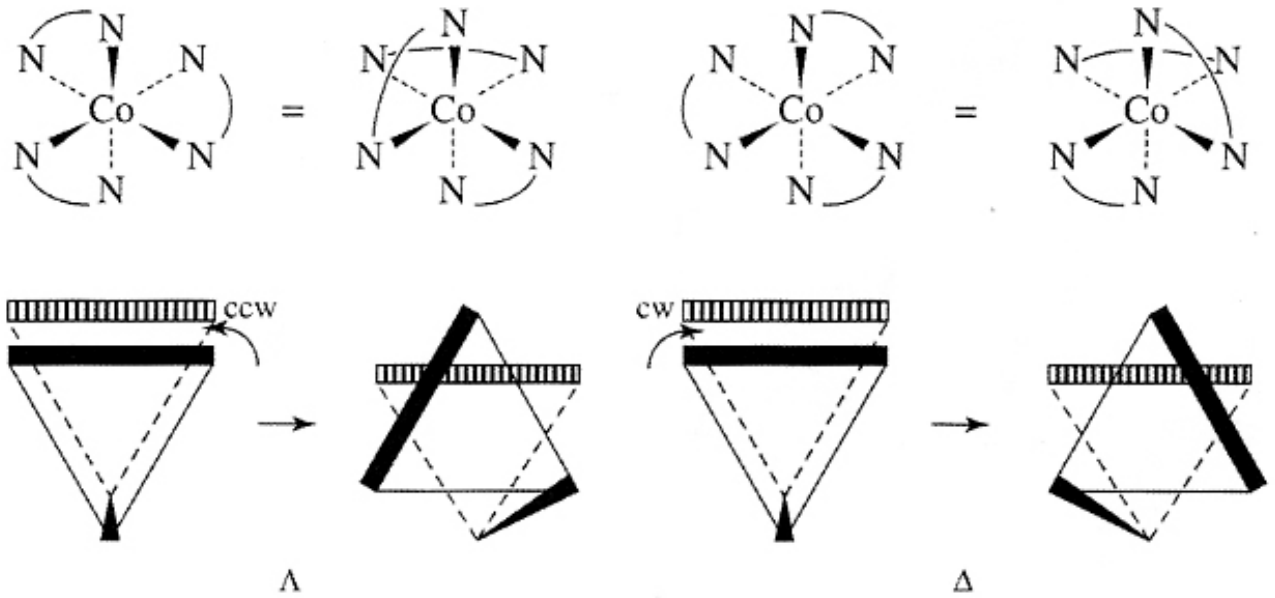
그림 9-13 왼쪽성(Λ)과 오른쪽성(Δ)의 킬레이트.

Isomerism – Stereoisomers: Combination of Chelate Rings (∧, Δ)

Procedure for Determining Handedness

그림 9-14 손대칭성을 결정하는 방법.

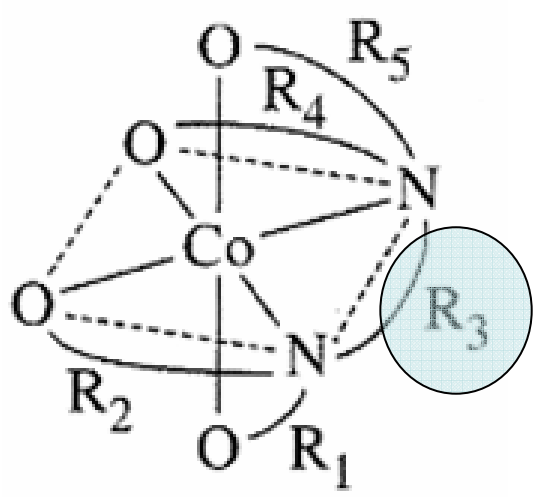
1. 분자를 돌려서 뒤쪽의 삼각형 관계에 있는 3개의 N(중심 금속과 점선으로 연결되어 있음) 중 윗부분의 2개가 고리를 형성하도록 위치시킨다.
2. 앞쪽 3개의 N(중심 금속과 꺽쇠 표시로 연결되어 있음)에 의해 만들어진 삼각형만을 태엽을 감듯이 회전시켜 앞과 뒤의 삼각형이 겹쳐지는 삼각기둥(trigonal prism) 모양을 만드는 것을 상상한다.
3. 태엽을 감듯 힘을 준 손을 놓았을 때 원래의 모습으로 돌아가는 회전 방향이 반시계 방향이면 람다(lamda, Λ) 이성질체이고, 원래의 모습으로 돌아가는 회전 방향이 시계 방향이면 델타(delta, Δ) 이성질체이다.



Isomerism – Stereoisomers: Combination of Chelate Rings (∧, Δ)

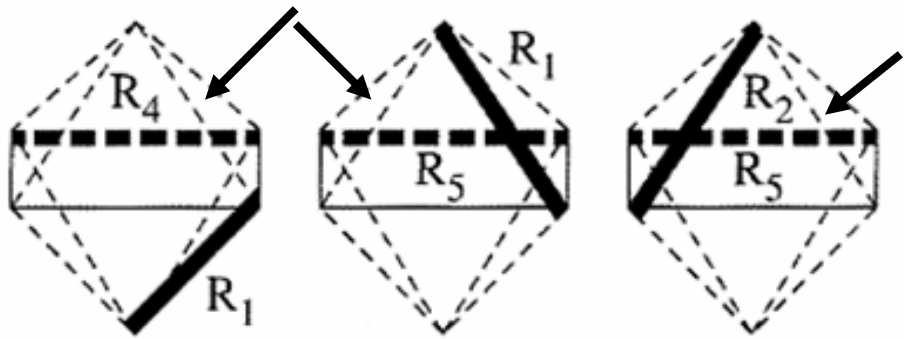
$CoEDTA^-$

Not coplanar, not connected at the same atom

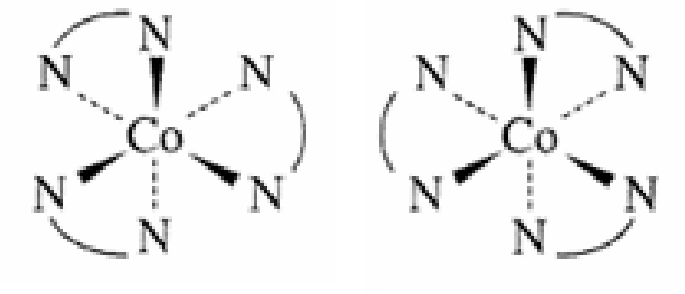


R1: ~~R2~~, ~~R3~~, R4, R5

R2: ~~R1~~, ~~R3~~, ~~R4~~, R5



∧ Δ ∧



∧ Δ

∧Δ∧, ∧∧Δ, or Δ∧∧

Isomerism – Stereoisomers: Lignad Ring Conformation

Chelate Ring Conformation (λ, δ)

Ex) ethylenediamine (en) :

1st line – conneting atoms bonded to the metal
2nd line – conneting two carbon atoms

1st → 2nd : counterclockwise → λ
1st → 2nd : clockwise → δ

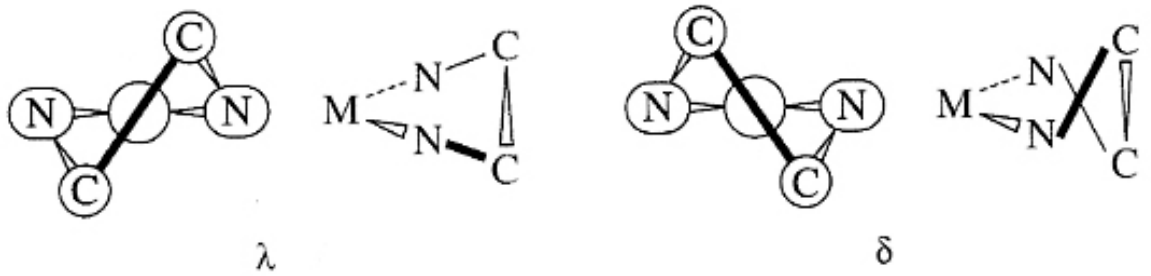


그림 9-16 킬레이트 고리의 뒤틀림 구조들.

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

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

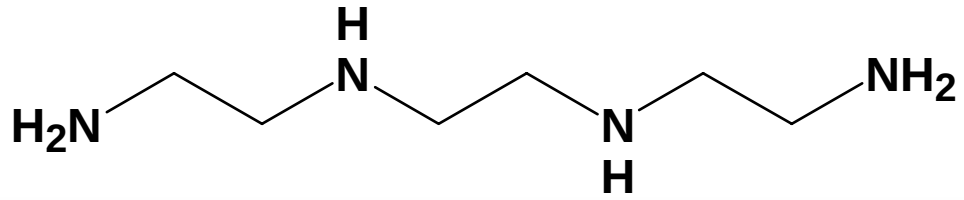
$\Delta\delta\delta$-$[Co(en)_3]^{3+}$

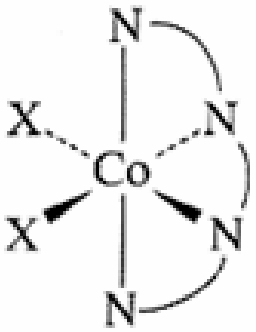
actually, in solution λ ←→ δ intercoversion

in soln, δδλ is most abundant in Λ form

Isomerism – Stereoisomers: Lignad Ring Conformation

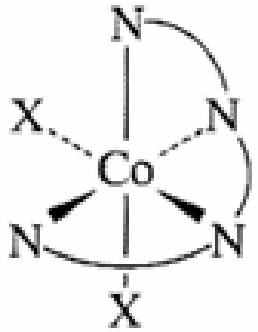
6 CN ; Octahedron, Triethylentetraamine





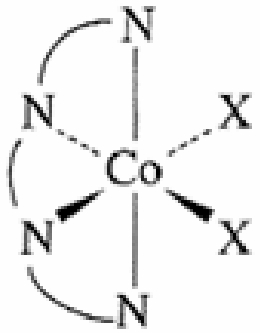
S S

Δ



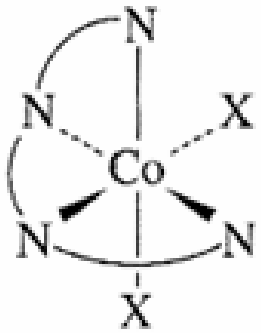
S S

Λ



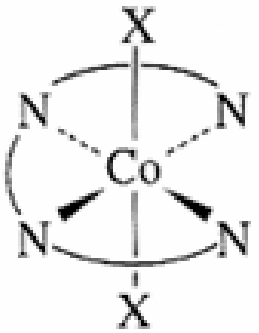
R R

Λ



R R

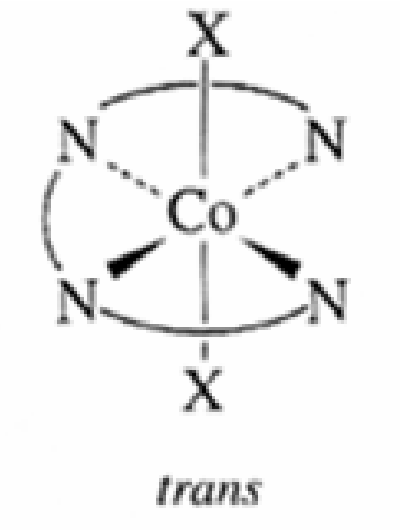
Δ



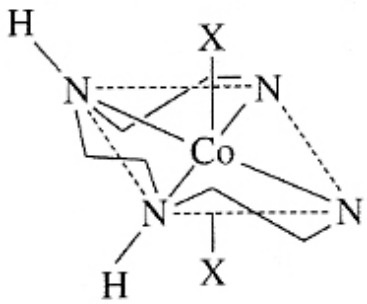
α β *trans*

Isomerism – Stereoisomers: Lignad Ring Conformation

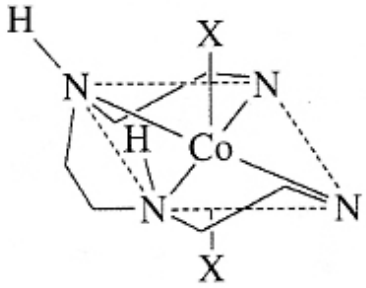
6 CN ; Octahedron, Triethylentetraamine



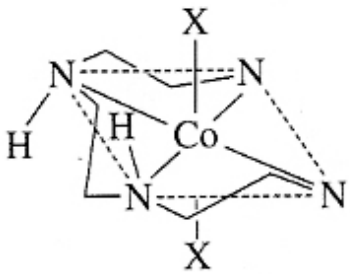
Chelate Ring Conformation (λ, δ)



δδ



δλ

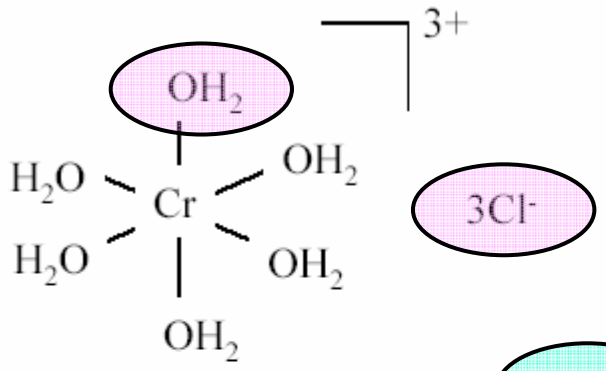


λλ

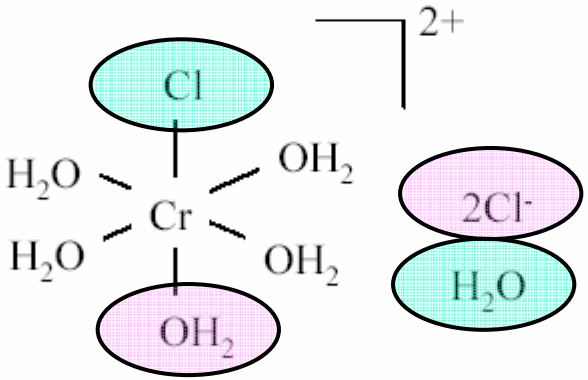
그림 9-17 트랜스-$[CoX_2\ (trien)]^+$의 카이랄 구조.

Isomerism – Constitutional Isomers: Hydrate Isomers

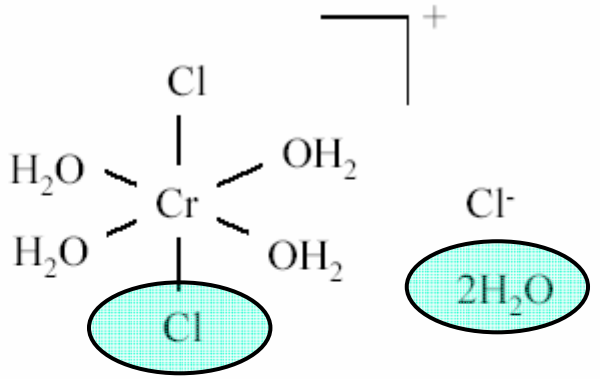
Hydrate Isomers: having water as either a ligand or an added part of the crystal structure



violet



blue-green

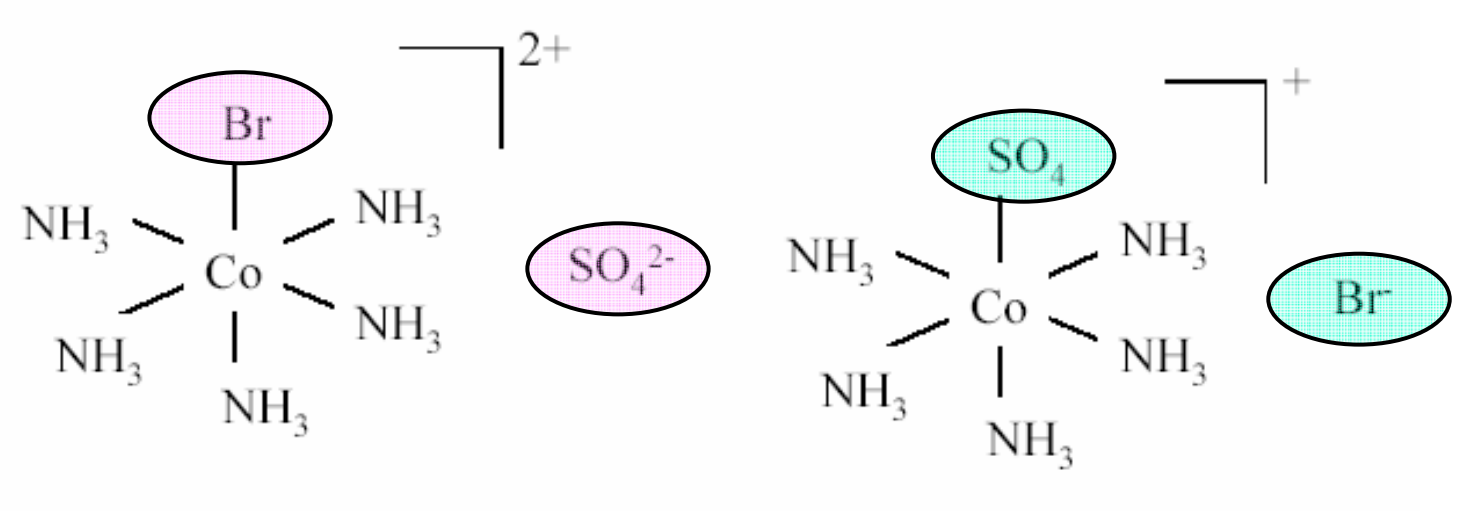


green

Tetraaquadichlorochromium(III) chloridedihydrate

Isomerism – Constitutional Isomers: Ionization Isomerism

Ionization Isomers: Exchange of ions between inside and outside coordination sphere



Isomerism – Constitutional Isomers: Coordination Isomerism

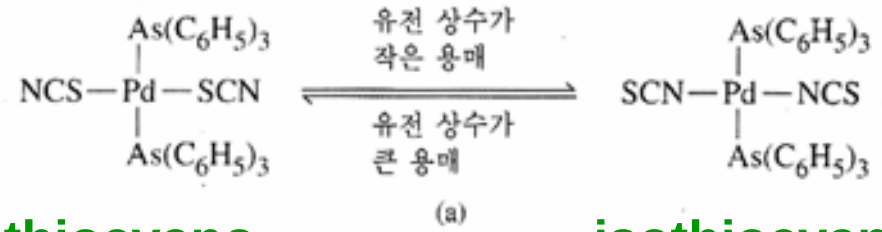
Coordination Isomers: require at least two metal

$[Co(en)_3]^{2+}[Cr(CN)_6]^{2-}$ $[Pt(NH_3)_4]^{2+}[PtCl_6]^{2-}$

$[Cr(en)_3]^{2+}[Co(CN)_6]^{2-}$ $[Pt(NH_3)_4Cl_2]^{2+}[PtCl_4]^{2-}$

Isomerism – Constitutional Isomers: Linkage (ambidentate) Isomerism

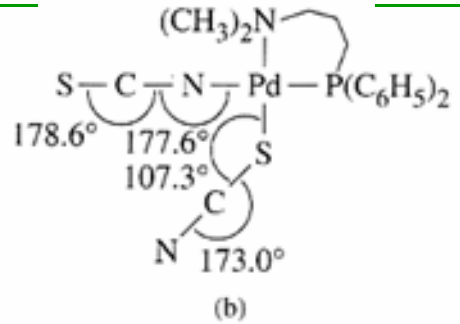
Linkage Isomers: Compounds containing ambidentate ligand



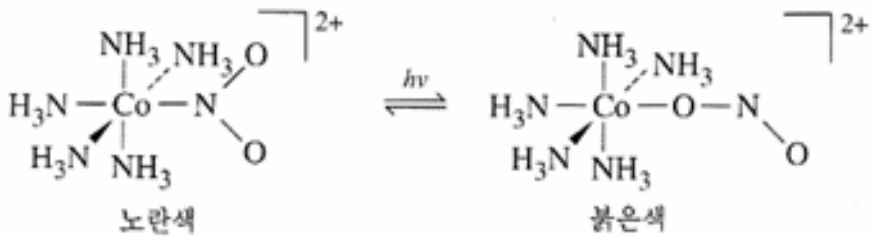
thiocyano

isothiocyano

thiocyanate

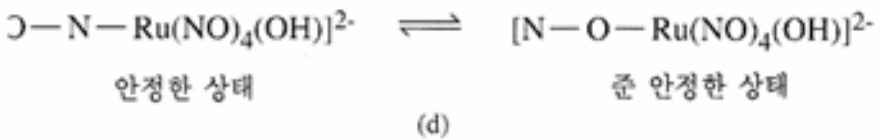


nitrite



nitro

nitrito



Coordination Numbers and Structures

Structures vs Properties.

Factors for Structures

1. Number of Bonds
   Bond formation is usually exothermic.
   So stability
2. VSEPR
3. Occupancy of d orbitals
   Square-planar vs Tetrahedral
4. Steric Effects
5. Crystal Packing Effects
   Crystalline Lattice vs Solution

What is common thing?
Which one is a dominant factor?

CN	Geometries
1	Rare
2	Linear
3	Trigonal-plane
4	**Tetrahedron**, **Square-plane**
5	Trigonal bipyramid, Square pyramid
6	**Octahedron**, Trigonal prosm
7	Pentagonal bipyramid, Capped trigonal prism, Capped octahedron
8≤	Known up to 16 CN

Coordination Numbers and Structures

Oxidation States of Transition Metals

	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

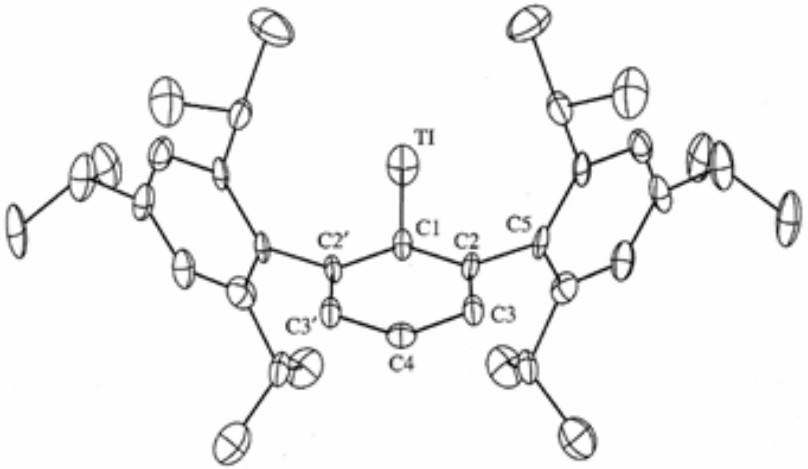
Coordination Numbers and Structures

CN = 1,2, and 3

CN = 1, Rare

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
								109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr



Coordination Numbers and Structures

CN = 1,2, and 3

CN = 2, Rare, Linear ($D_{\infty h}$)

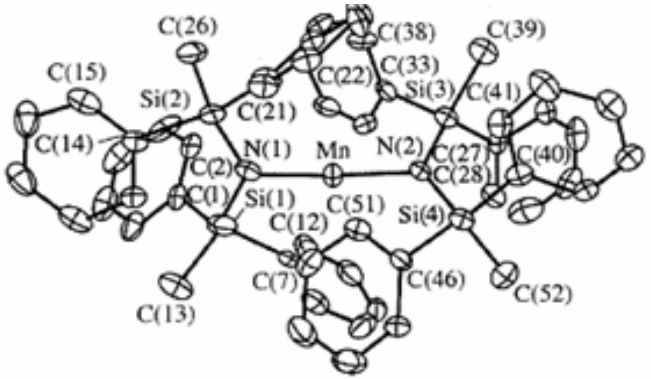
Mostly d^{10} metals, Ag(I), Cu(I), Au(I), Hg(II)

d^5, d^6, d^7

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	22	23	24	25	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37	38						44	45	46	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
										79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
										111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

												64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
												96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Examples of CN = 2



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

$H_3N-Ag-NH_3]^+$

$Cl-Cu-Cl]^-$

$NC-Hg-CN$

$CN-Au-CN]^-$

Large Ligands can induce a linear arrangement

Coordination Numbers and Structures

CN = 1,2, and 3

CN = 3, Rare, Trigonal planar (D_{3h})
Mostly d^{10},
PPh_3, $N(SiMe_3)_2$,
Bulky enough, Steric effect vs Electroic structure

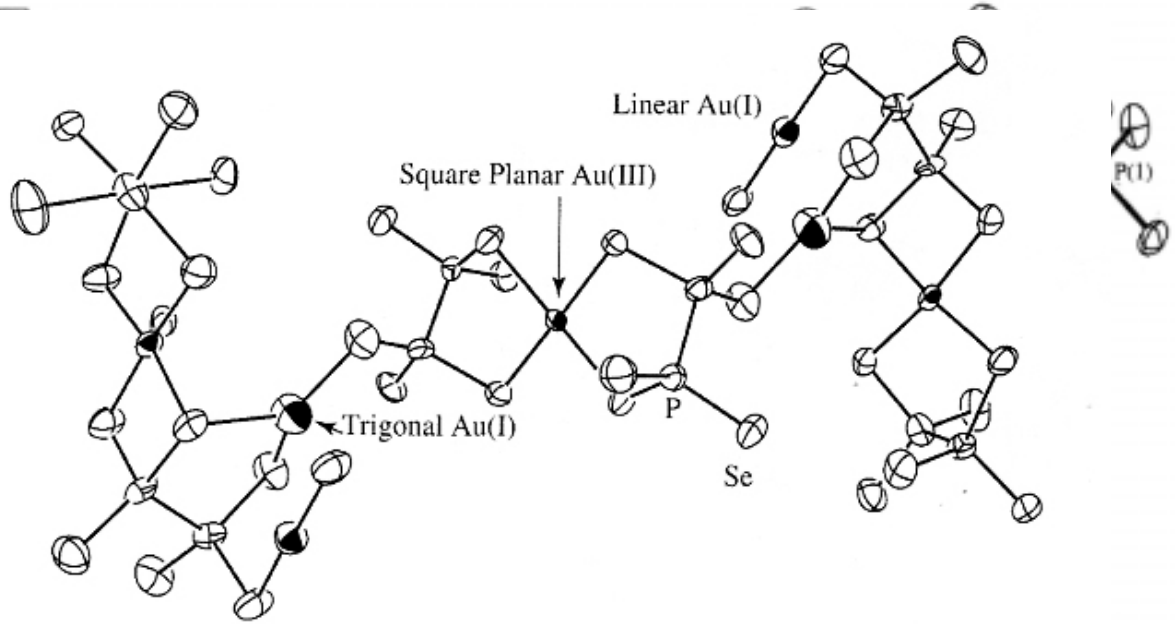
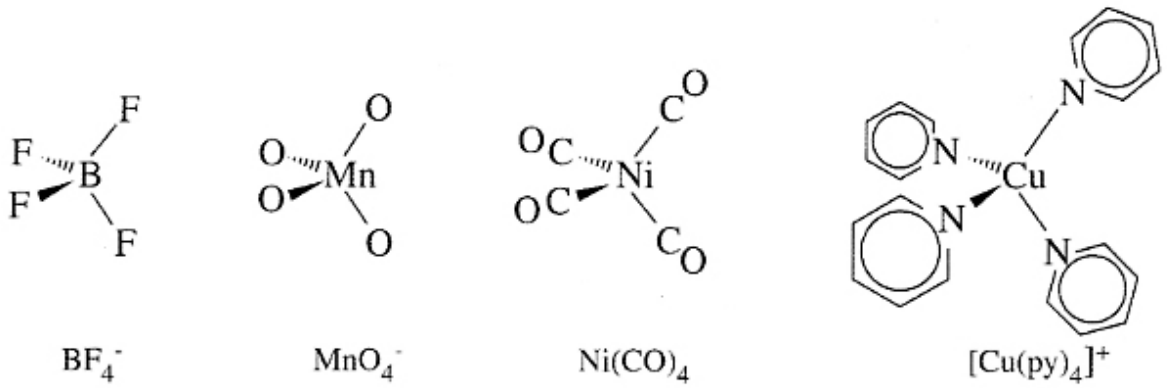


그림 9-24 $K_2Au_2P_2Se_6$, 세 가지 서로 다른 구조를 가지는 Au을 포함하는 화합물. 검은색 표시된 구, Au; 큰 무색 구, Se; 작은 무색 구, P. $[P_2Se_6]^{4-}$ 이온이 Au(I) 이온을 선형과 삼각형 구조로 연결하고 Au(III) 이온을 평면사각형 구조로 연결한다. 이 구조는 긴 사슬 모양을 하면서 K^+ 이온을 포함하는 긴 채널(channel)을 이루면서 적층되며 결정을 이룬다.
(K. Chordroudis, T. J. McCarthy, 그리고 M. G. Kanatzidis의 *Inorg Chem.* **1996**, *35*, 3451에서 발췌함)

Coordination Numbers and Structures

CN = 4

CN = 4, Tetrahedral (T_d) Squre-planar(D_{4h})
Tetrahedral (T_d) ; very common,



BF_4^- MnO_4^- $Ni(CO)_4$ $[Cu(py)_4]^+$

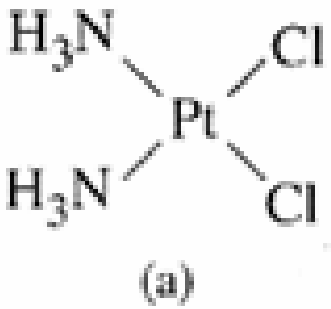
그림 9-25 정사면체 구조를 가지는 착화합물들.

Coordination Numbers and Structures

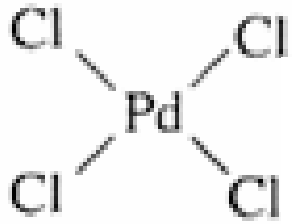
CN = 4

CN = 4, Tetrahedral (T_d) Squre-planar(D_{4h})

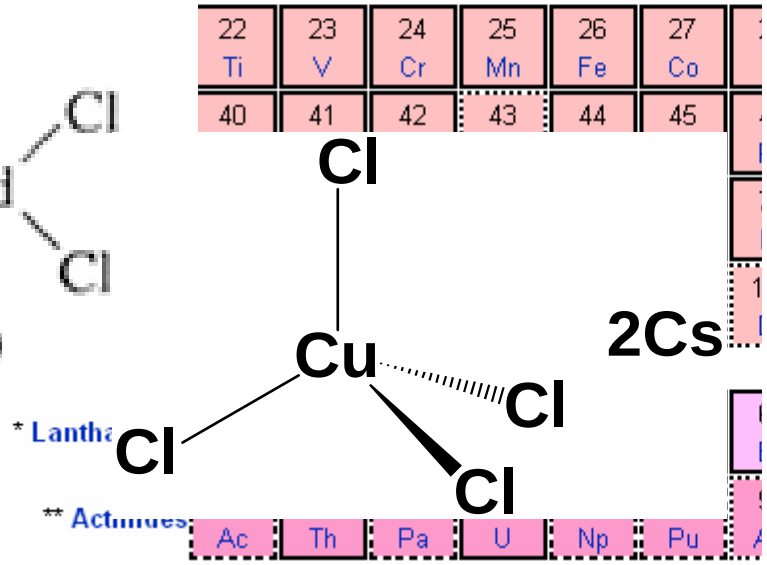
Squre-planar(D_{4h}) ; mostly d^8 (Pd(II), Pt(II), Ni(II), Ag(III), Ir(I) Rh(I))

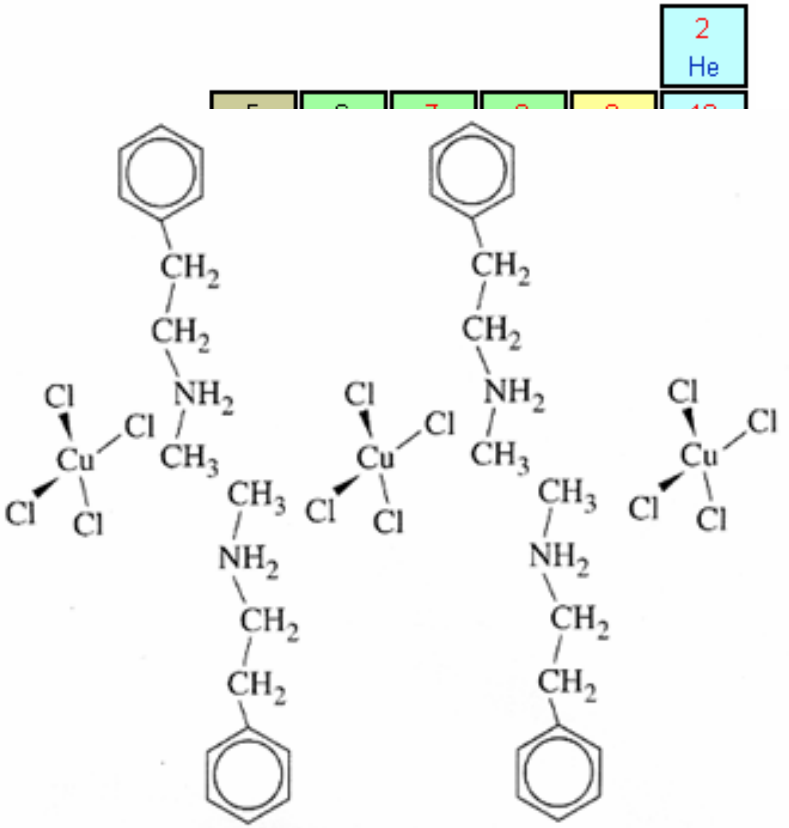


(a)



(b)





Coordination Numbers and Structures

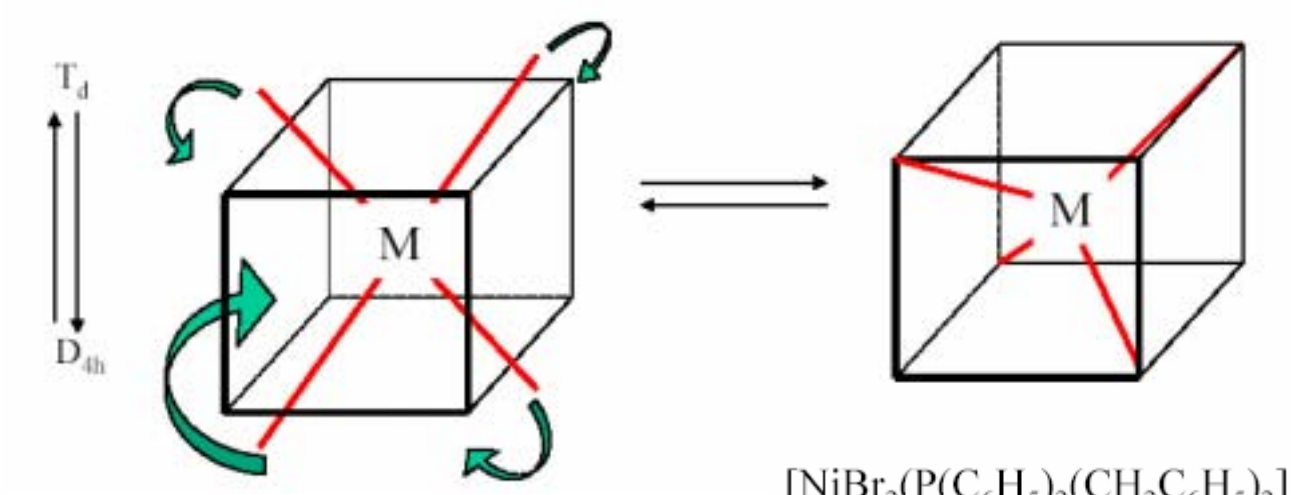
CN = 4

CN = 4, Tetrahedral (T_d) Squre-planar(D_{4h})

Squre-planar(D_{4h}) ; mostly d^8 (Pd(II), Pt(II), Ni(II), Ag(III), Ir(I) Rh(I))

Tetrahedral vs Square-planar

Counterion, Crystal Packing



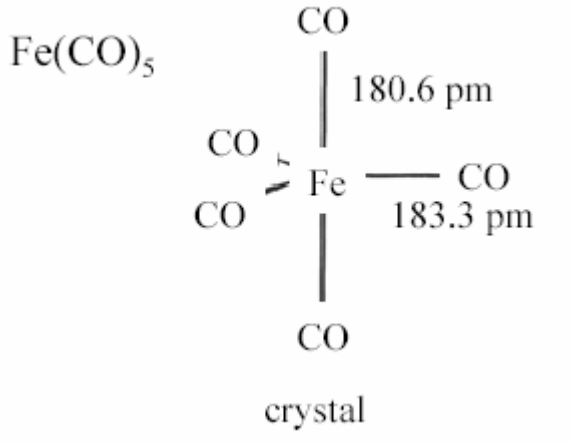
ΔE is not big.

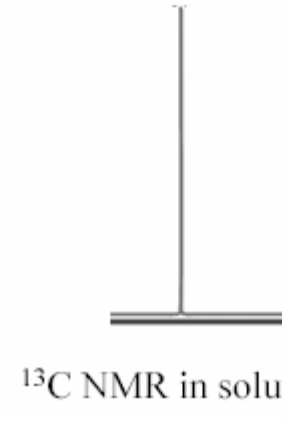
$[NiBr_2(P(C_6H_5)_2(CH_2C_6H_5)_2]$: both T_d and D_{4h} in the same crystal

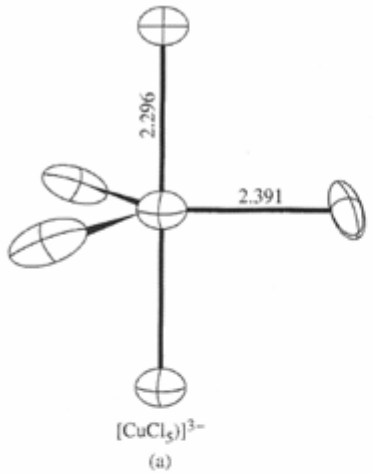
Coordination Numbers and Structures

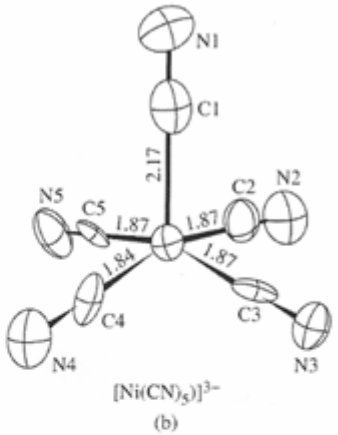
CN = 5

CN = 5, Trigonal bipyramid (D_{3h}), Square pyramid (C_{4v})

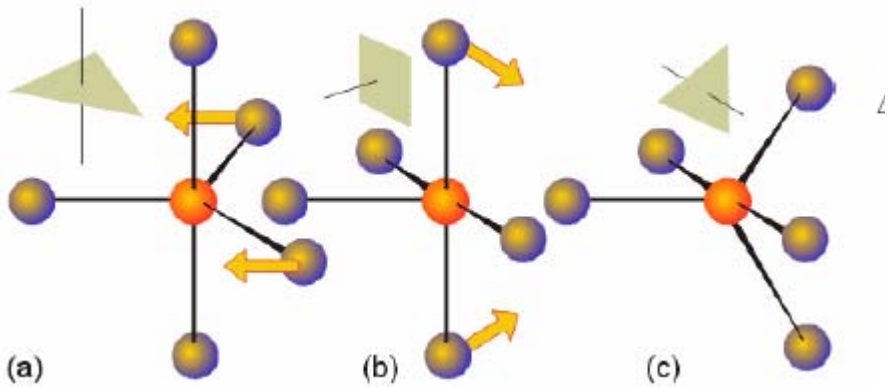


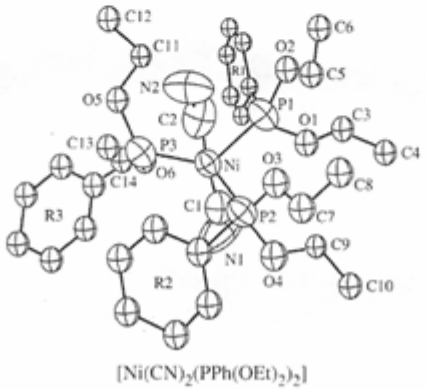






Fluxional behavior.

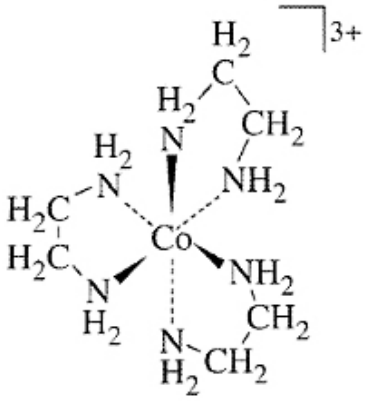




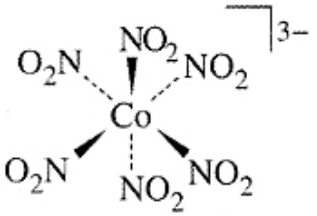
Coordination Numbers and Structures

CN = 6

CN = 6, Octahedral (O_h) most common



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



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

그림 9-28 정팔면체 구조의 착 화합물들.

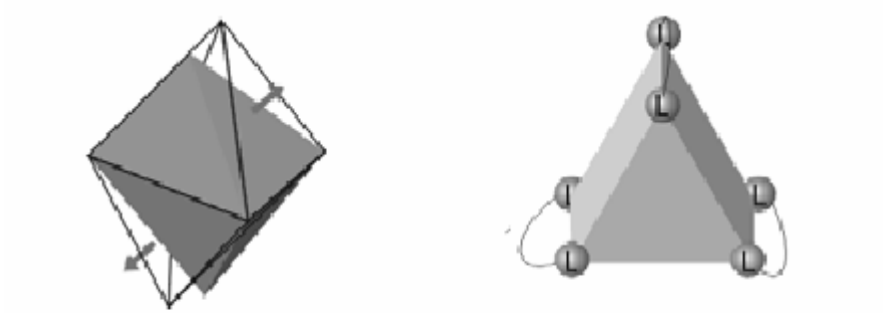
잡아당김 눌려짐

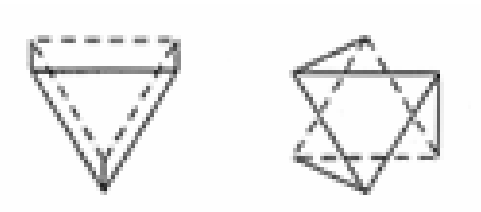
그림 9-29 정팔면체의 사각형 일그러짐.

Coordination Numbers and Structures

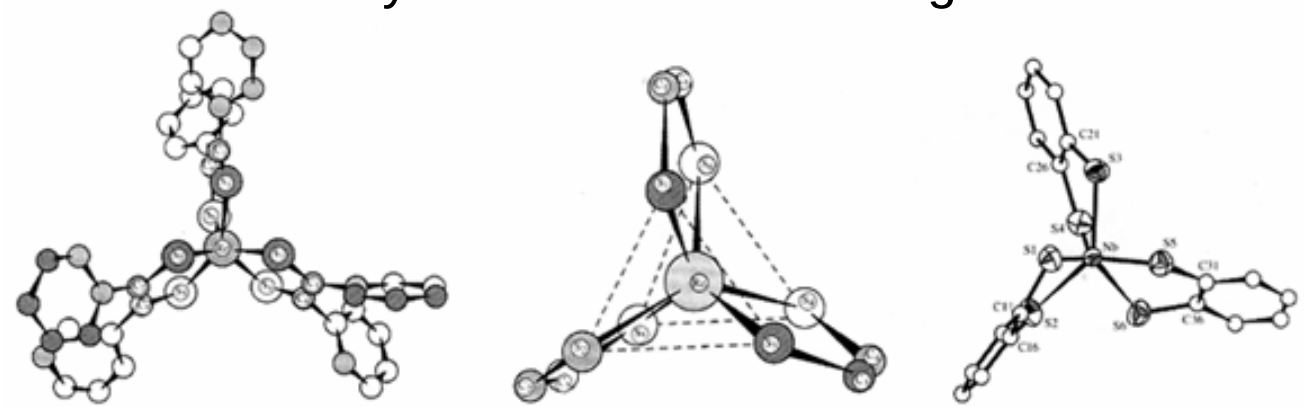
CN = 6

CN = 6, Octahedral (O_h) to Trigonal Prism (D_{3h})





Usually with three bidentate ligands

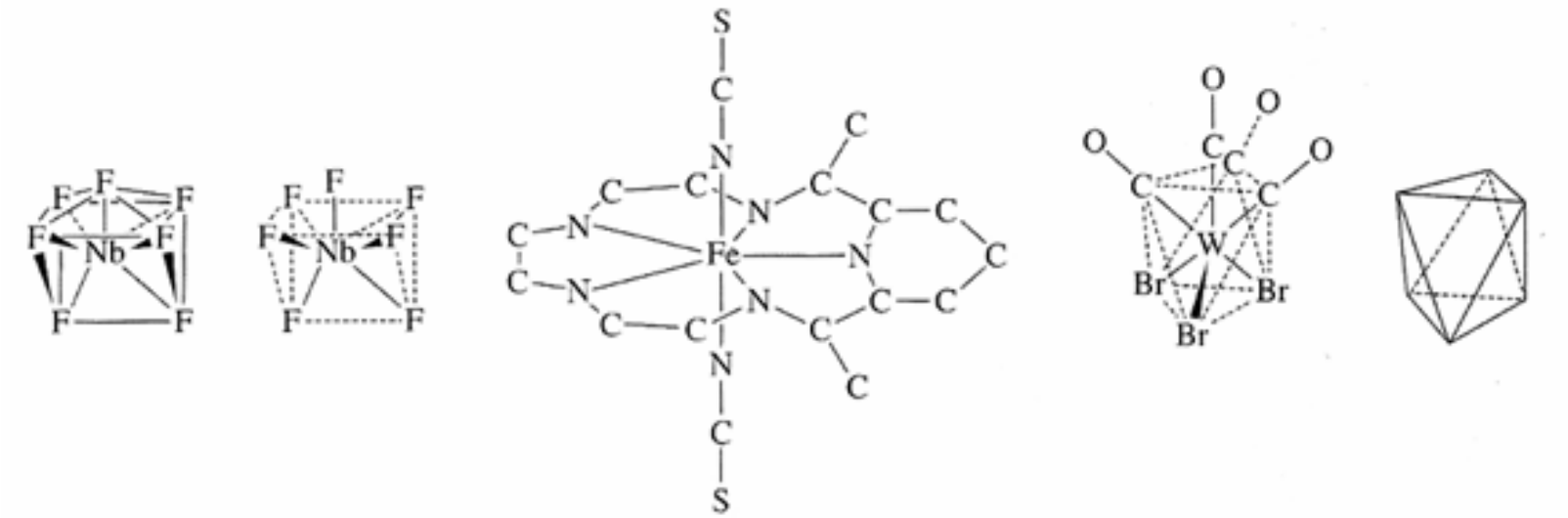


π Interactions between adjacent sulfur atoms

Coordination Numbers and Structures

CN = 7

CN = 7, Pentagonal bipyramid (O_h), Capped trigonal prism, Capped octahedron



Capped trigonal prism Pentagonal bupyramid Capped octahedron

Different counterion, steric requirment

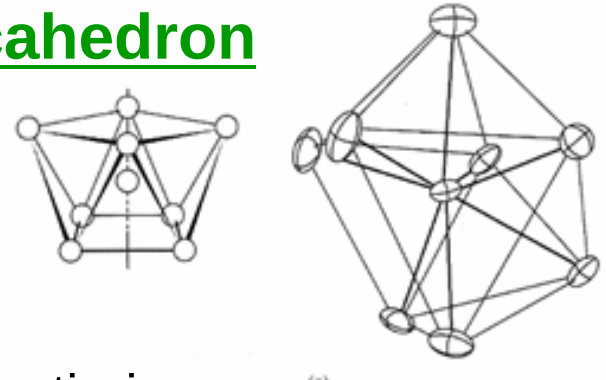
Coordination Numbers and Structures

CN = 8

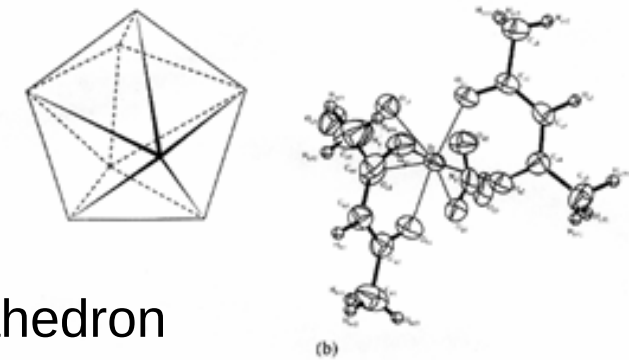
CN = 8, Square antiprism, Dodecahedron

Eight coordination is rare in the first row transition metals

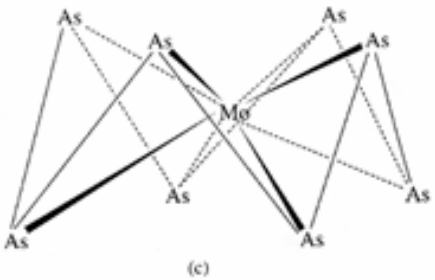
Central ion must be large in order to accommodate eight-coordination



Square antiprism



Dodecahedron



Compressed Square antiprism

Coordination Numbers and Structures

CN ≥ 8

CN ≥ 8, known up to 16, not common

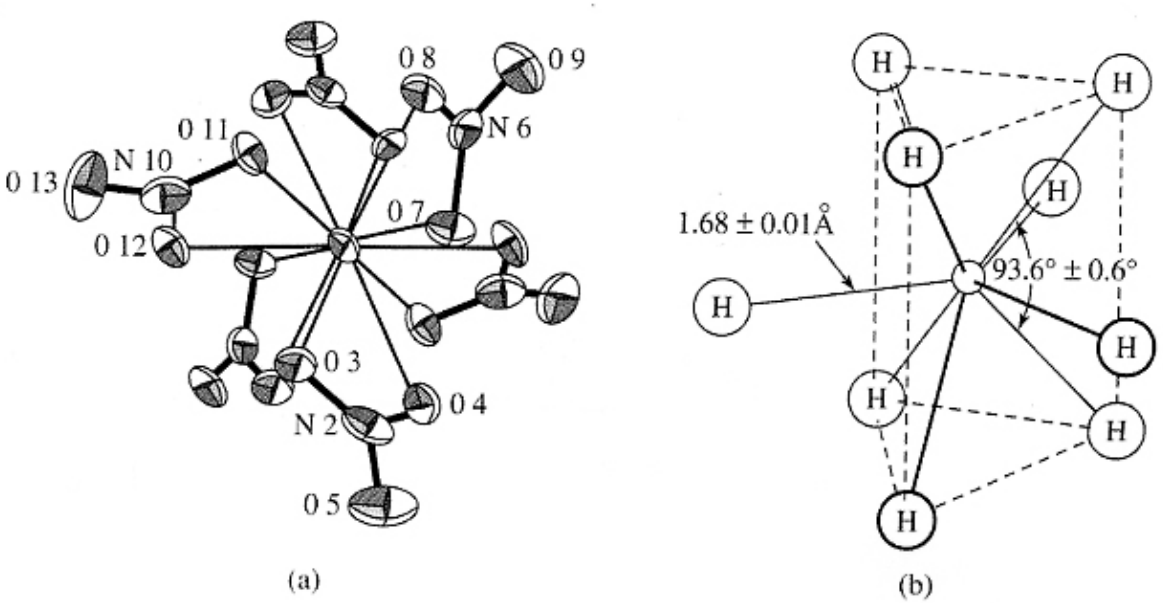
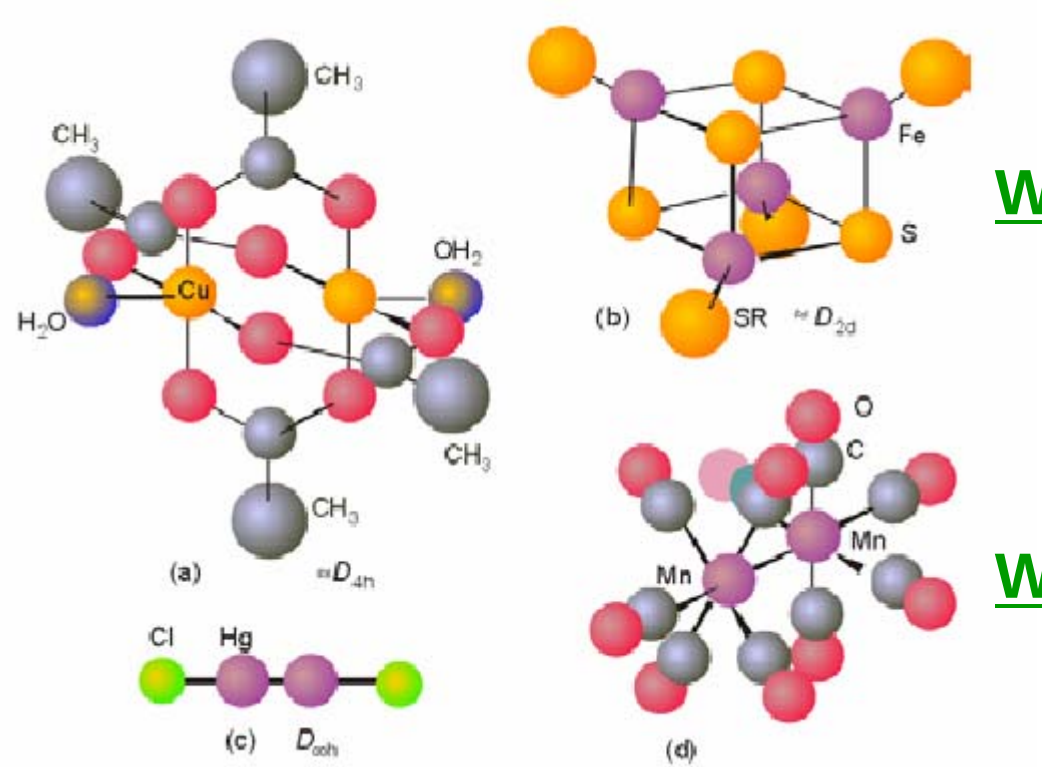


그림 9-33 큰 배위수를 가지는 배위 화합물들. (a) $[Ce(NO_3)_6]^{3-}$, 나이트레이트(nitrate) 리간드가 두 자리 리간드로 결합. (T. A. Beinnecke와 J. Delgaudio의 *Inorg. Chem.* **1968**, *7*, 715에서 발췌함) (b) [ReH9]2-, 덧씌운 삼각 프리즘(capped trigonal prism) 구조. (S. C. Abrahams, A. P. Ginsberg, 그리고 K. Knox의 *Inorg. Chem.* **1964**, *3*, 558에서 발췌함)

Multimetallic Compexes



Without direct M-M bond

With direct M-Mm bond