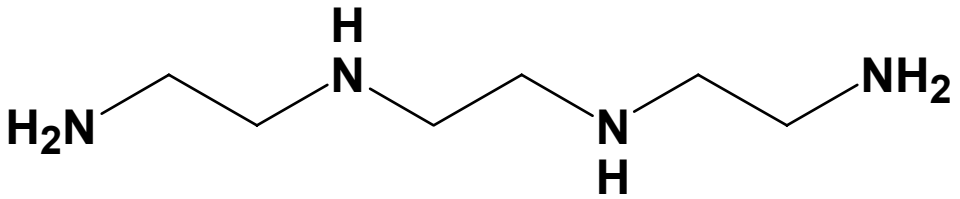
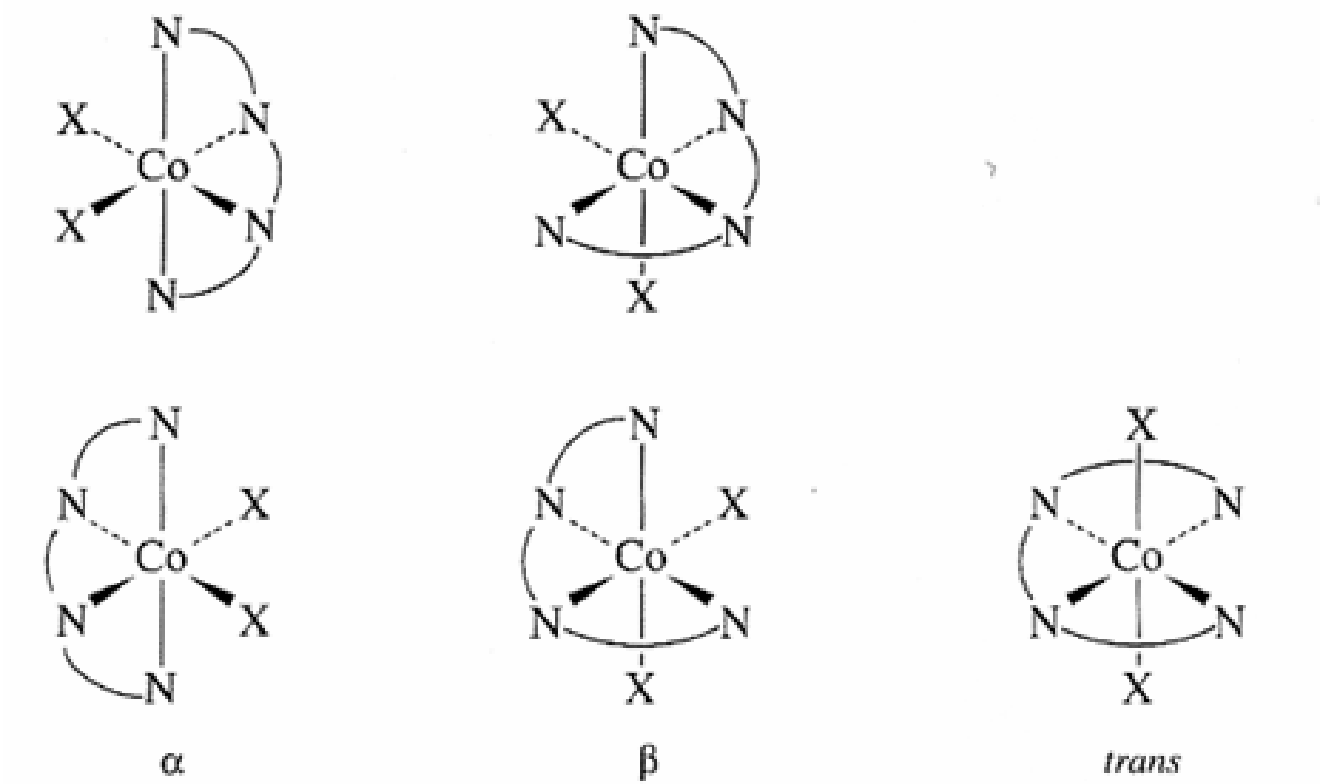
Isomerism - Stereoisomers

6 CN ; Octahedron, Triethylentetraamine





No coplanar rings

Two coplanar rings

Three coplanar rings

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

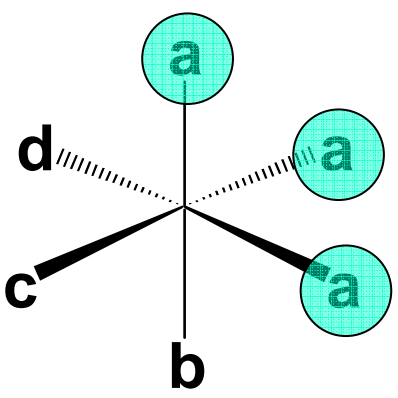
주: 대문자로 표기된 리간드는 킬레이트 리간드이고, 소문자로 표기된 것은 한 자리 리간드이다.

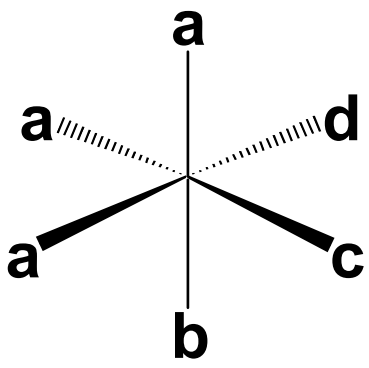
Isomerism - Stereoisomers

Number of possible Isomers

Ma_3bcd

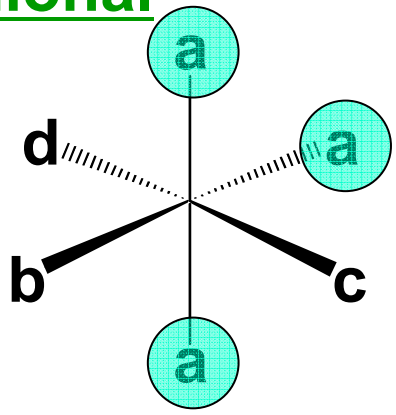
facial

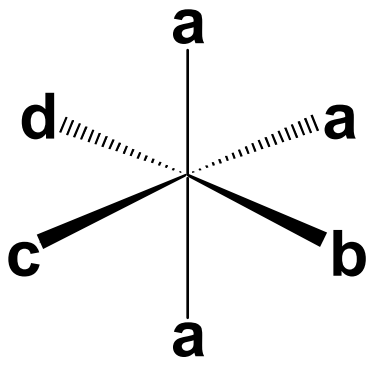


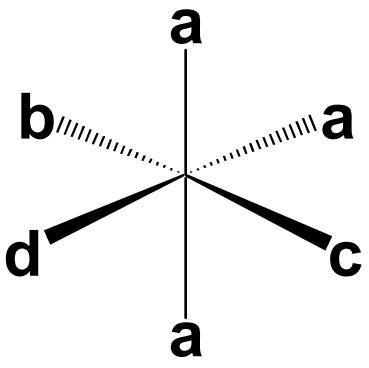


no mirror plane

meridional

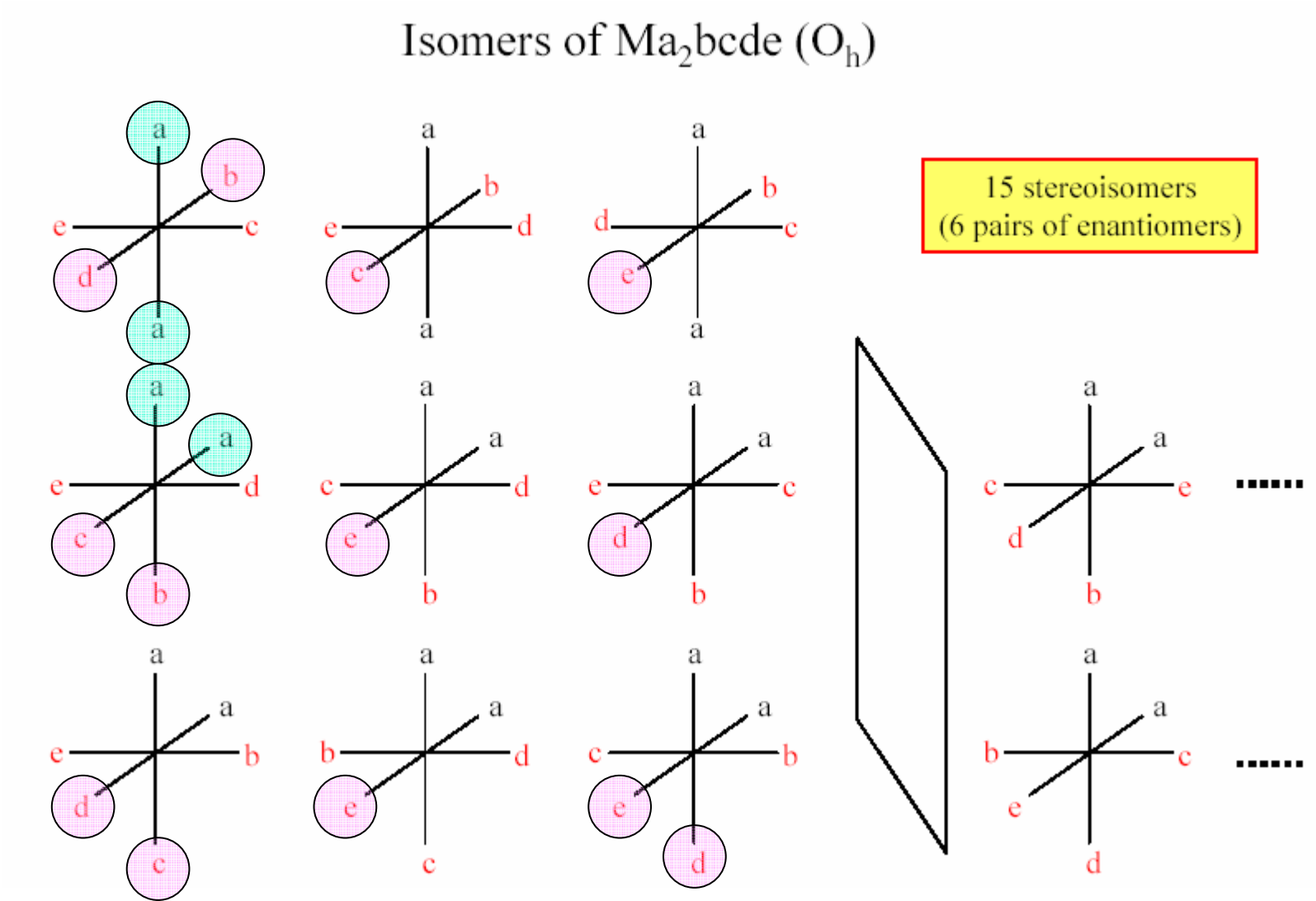






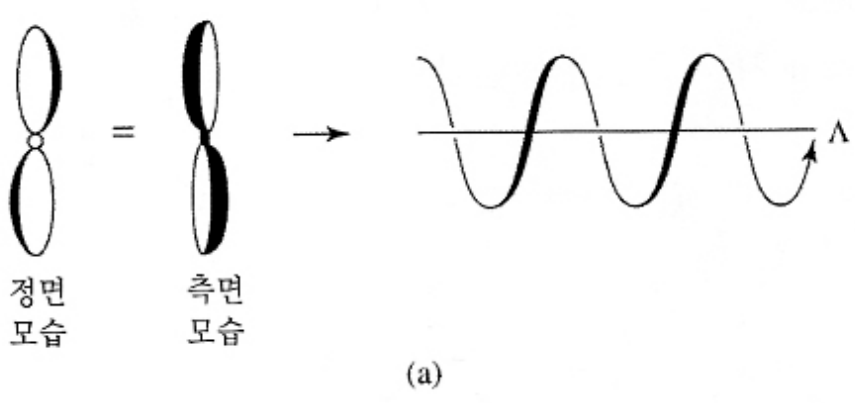
Isomerism - Stereoisomers

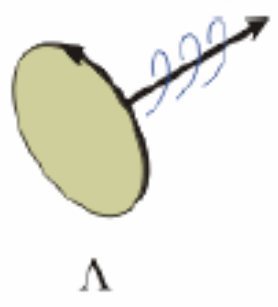
Number of possible Isomers



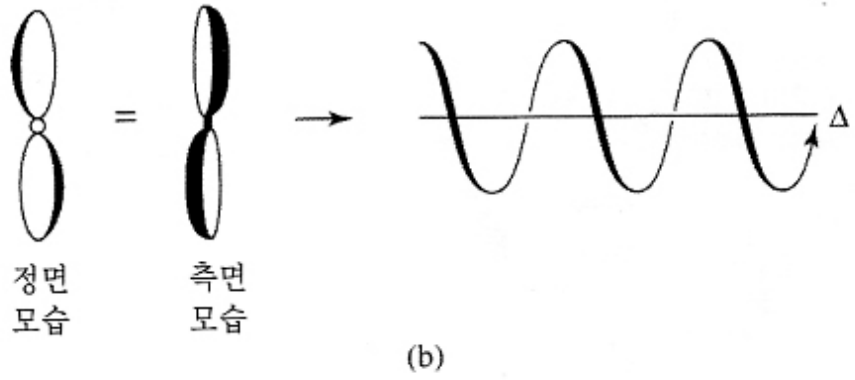
Isomerism – Stereoisomers: Combination of Chelate Rings (Λ, Δ)

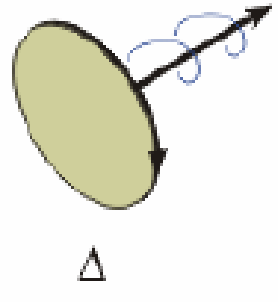
Handedness of chelate Rings





Lambda





Delta

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)

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

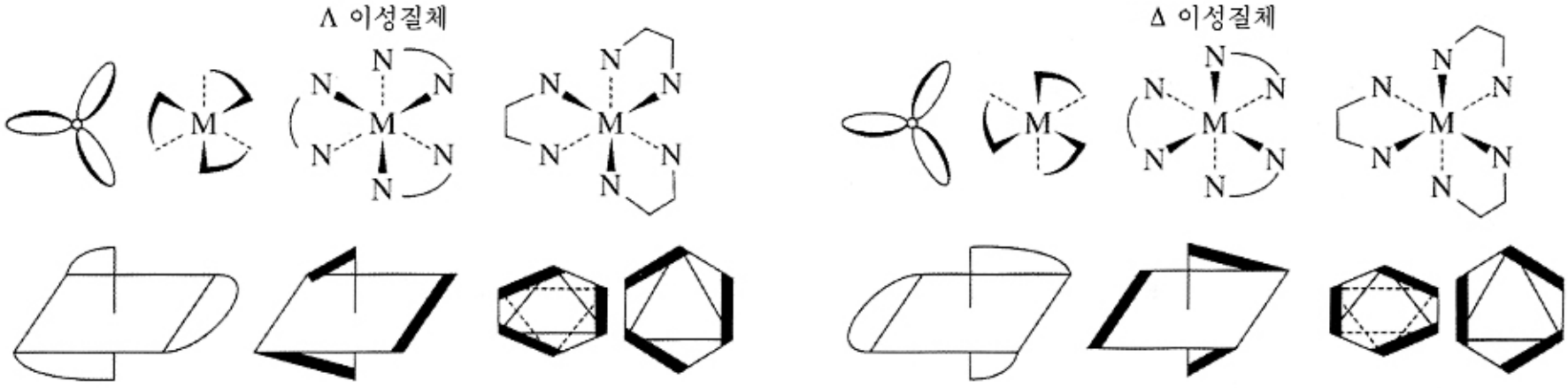


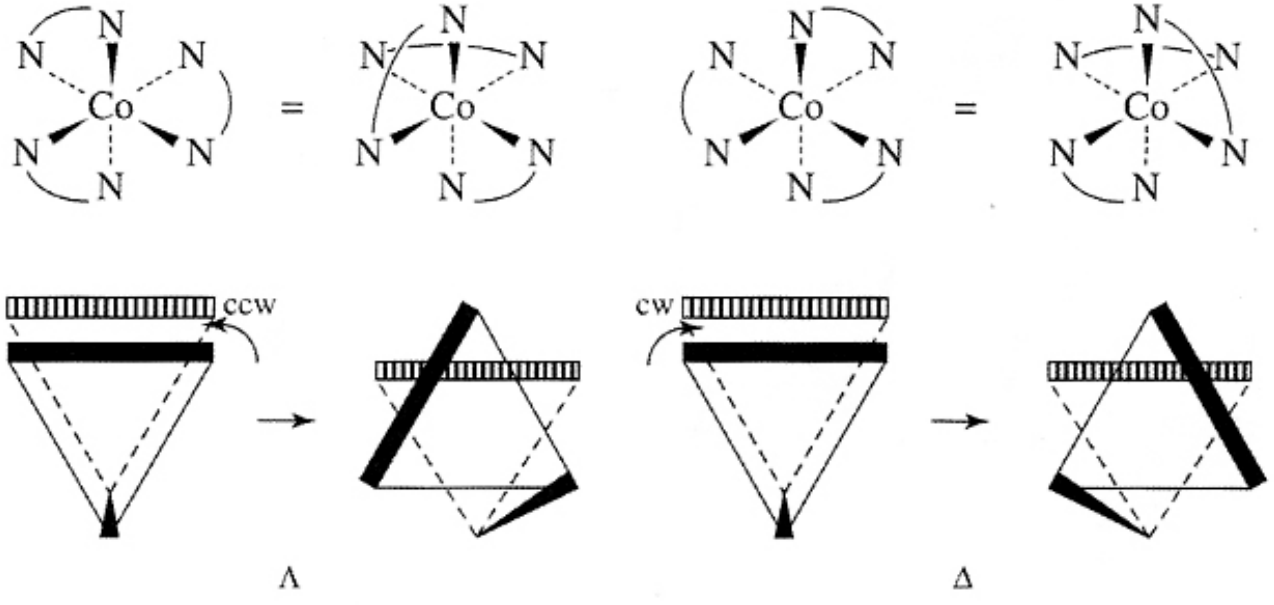
그림 9-13 왼쪽성(Λ)과 오른쪽성(Δ)의 킬레이트.

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

Procedure for Determining Handedness

그림 9-14 손대칭성을 결정하는 방법.

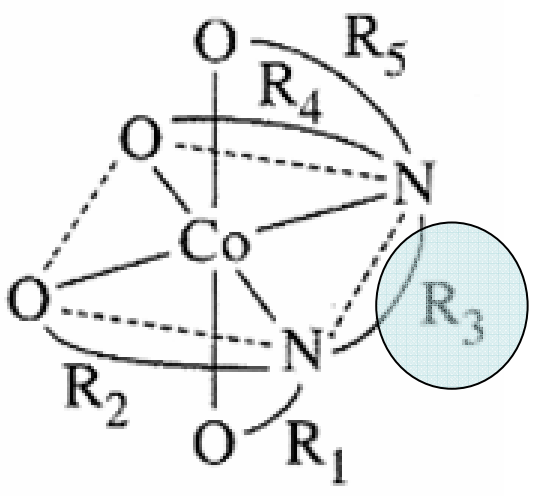
1. 분자를 돌려서 뒤쪽의 삼각형 관계에 있는 3개의 N(중심 금속과 점선으로 연결되어 있음)중 윗부분의 2개가 고리를 형성하도록 위치시킨다.
2. 앞쪽 3개의 N(중심 금속과 꺽쇠 표시로 연결되어 있음)에 의해 만들어진 삼각형만을 태엽을 감듯이 회전시켜 앞과 뒤의 삼각형이 겹쳐지는 삼각기둥(trigonal prism) 모양을 만드는 것을 상상한다.
3. 태엽을 감듯 힘을 준 손을 놓았을 때 원래의 모습으로 돌아가는 회전 방향이 반시계 방향이면 람다(lamda, Λ) 이성질체이고, 원래의 모습으로 돌아가는 회전 방향이 시계 방향이면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



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

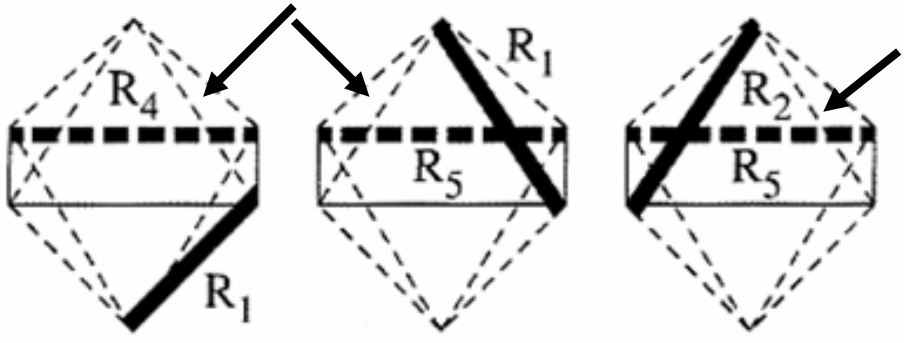
$CoEDTA^-$

Not coplanar, not connected at the same atom

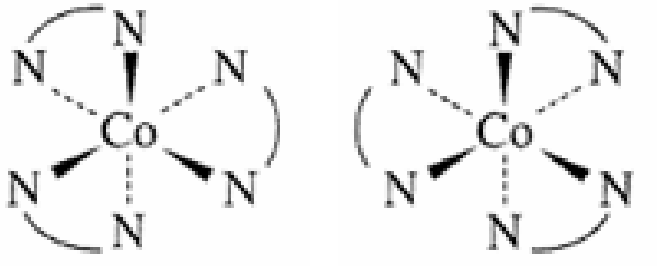


R1: ~~R2~~, ~~R3~~, R4, R5

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



∧ Δ ∧

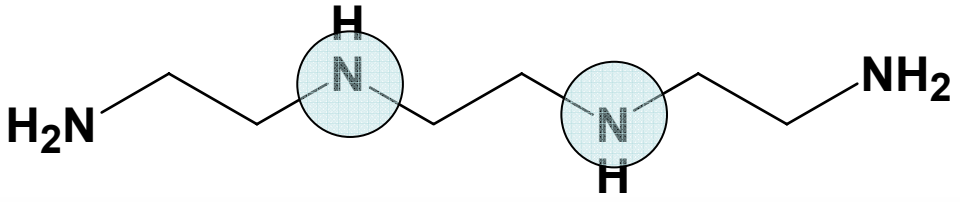


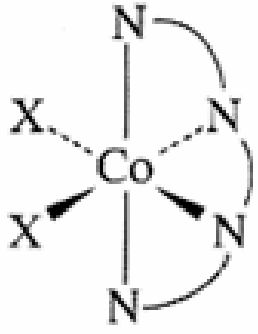
∧ Δ

∧Δ∧, ∧∧Δ, or Δ∧∧

Isomerism – Stereoisomers: Ligand Ring Conformation

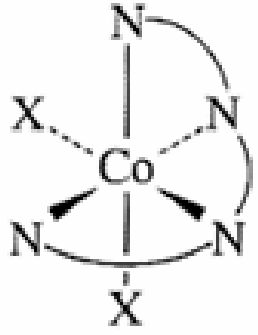
6 CN ; Octahedron, Triethylentetraamine





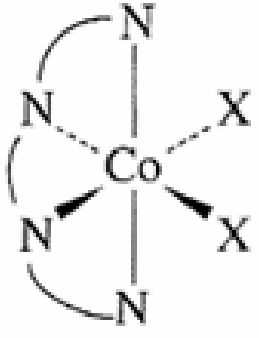
S S

Δ



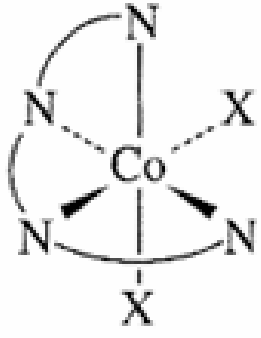
S S

Λ



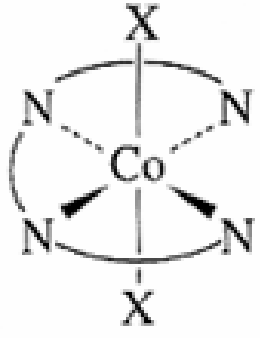
R R

Λ



R R

Δ



α

β

trans

Isomerism – Stereoisomers: Ligand 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

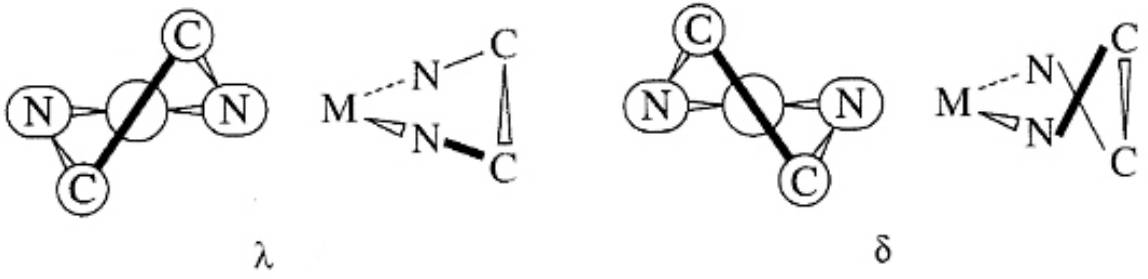


그림 9-16 킬레이트 고리의 뒤틀림 구조들.

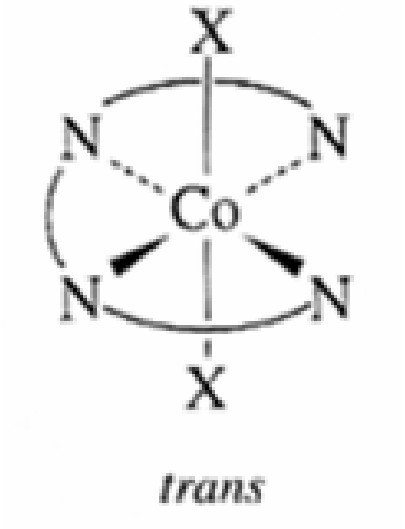
$[Co(en)_3]^{3+}$ $\Delta\lambda\lambda\lambda$-$[Co(en)_3]^{3+}$ $\Delta\delta\delta$-$[Co(en)_3]^{3+}$

more stable in calculation

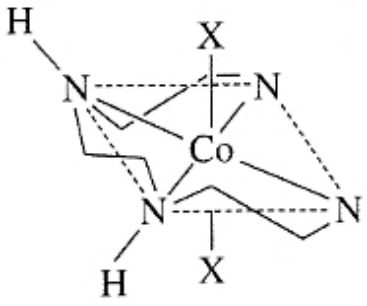
actually, in solution $\lambda \leftrightarrow \delta$ intercoversion in soln, $\delta\delta\lambda$ is most abundant in Λ form

Isomerism – Stereoisomers: Ligand Ring Conformation

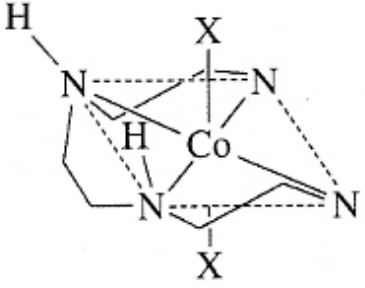
6 CN ; Octahedron, Triethylentetraamine



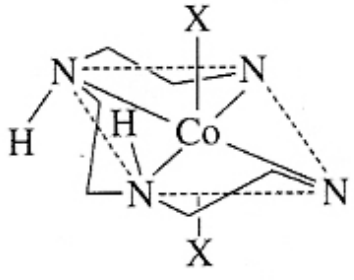
Chelate Ring Conformation (λ, δ)



δδ



δλ

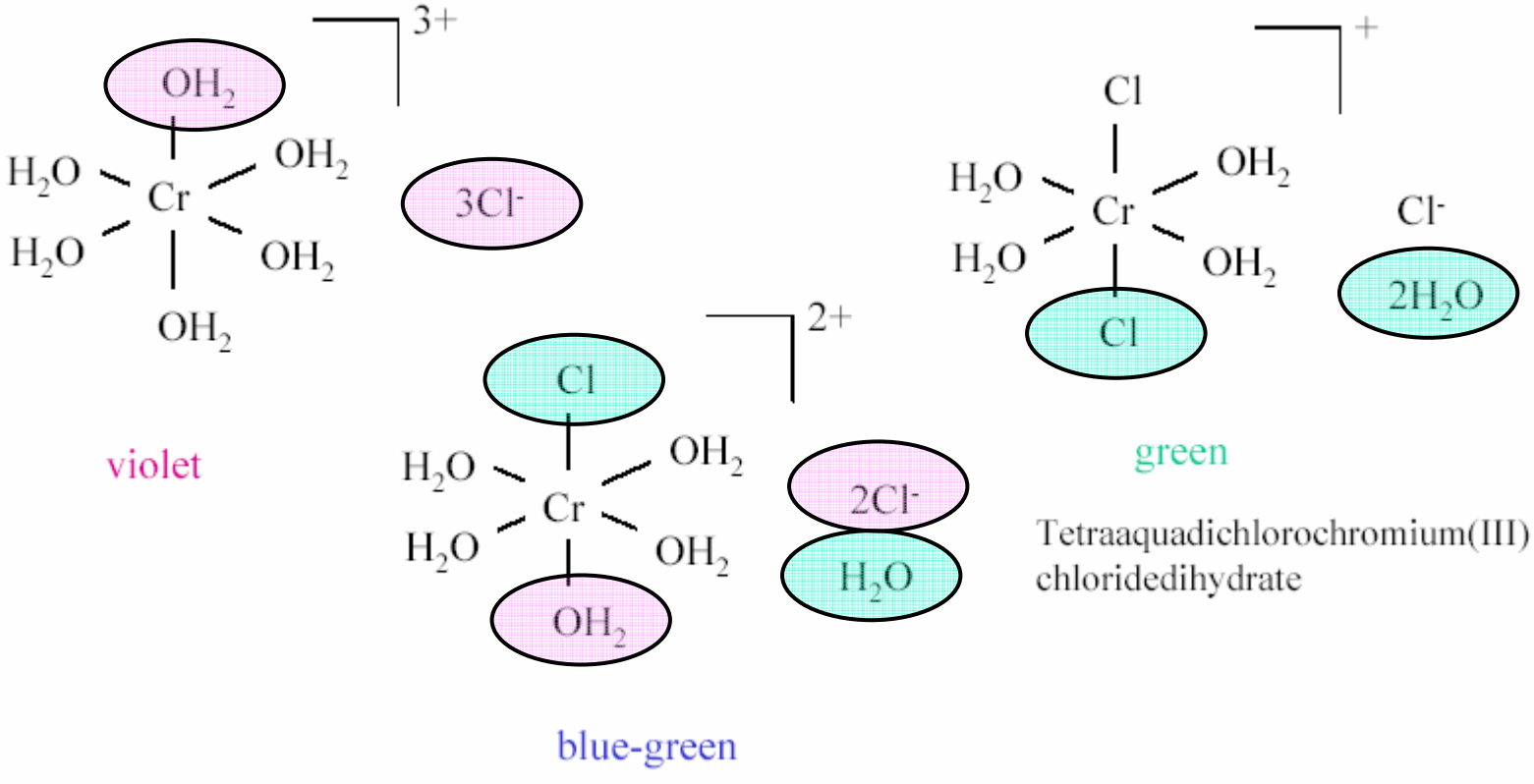


λλ

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

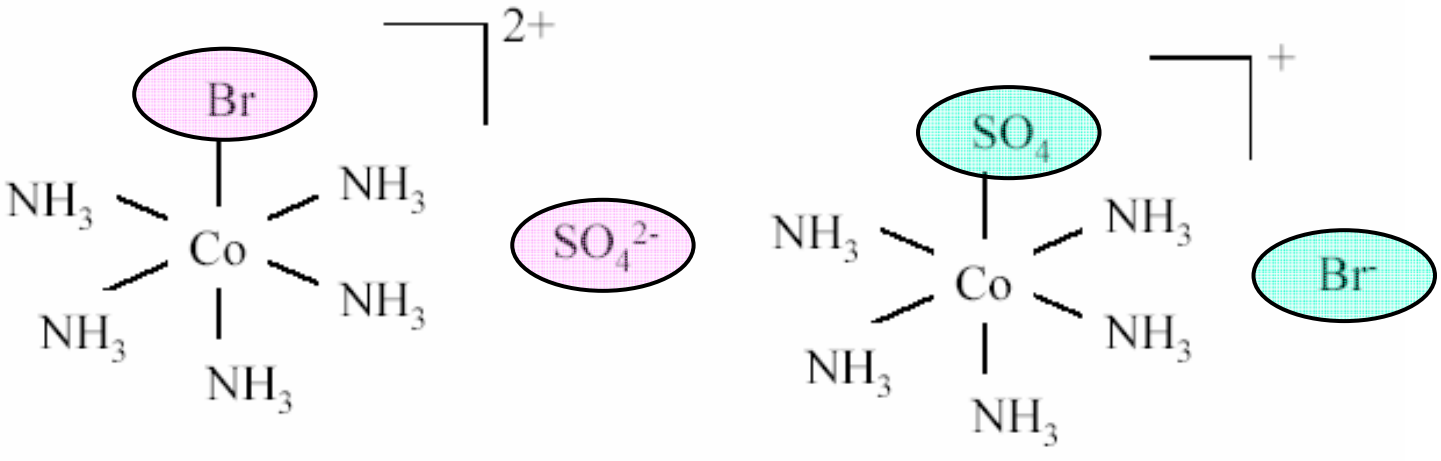
Isomerism – Constitutional Isomers: Hydrate Isomers

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



Isomerism – Constitutional Isomers: Ionization Isomerism

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



Isomerism – Constitutional Isomers: Coordination Isomerism

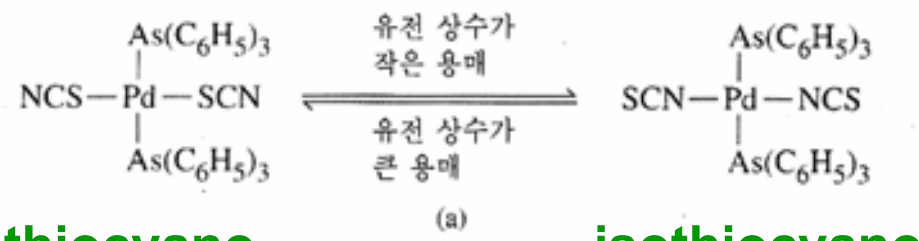
Coordination Isomers: require at least two metal

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

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

Isomerism – Constitutional Isomers: Linkage (ambidentate) Isomerism

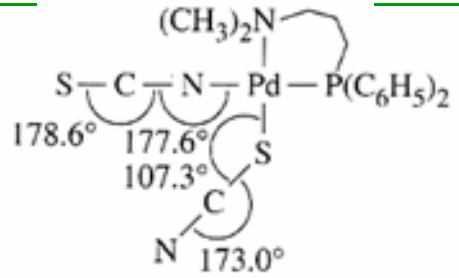
Linkage Isomers: Compounds containing ambidentate ligand



(a)

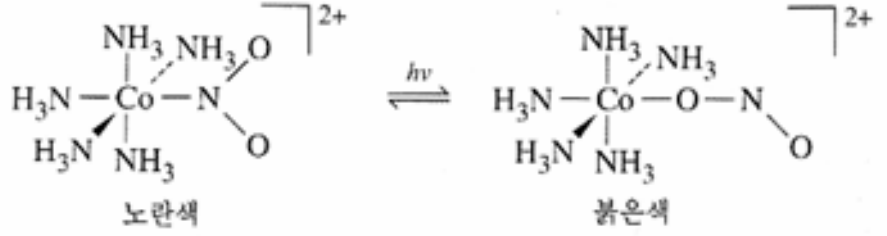
thiocyano — isothiocyano

thiocyanate



(b)

nitrite



(c)

nitro — nitrito

Isomerism – Separation and Identification of Isomers

Separation

Fractional Crystalization – packing, solubility, size, charge

Chiral Isomers
Resolution – chiral counterions

Identification

X-ray crystallography

Optical rotatory dispersion (ORD)

Circular dichroism (CD)

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

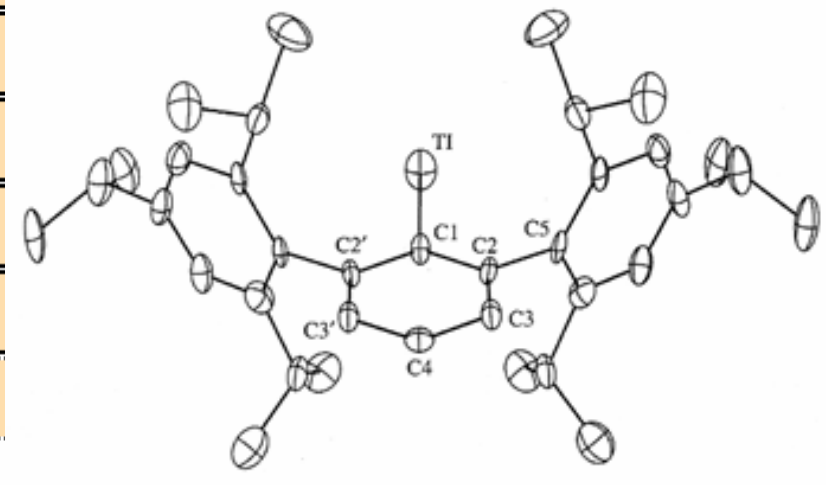
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
≤0			o	o	o	o	o	o	o	
+1			o	o	o	o	o	o	**O**	
+2		o	**O**	o	**O**	**O**	**O**	**O**	**O**	**O**
+3	**O**	o	o	**O**	o	**O**	**O**	o	o	
+4		**O**	o	o	**O**	o	o	o		
+5			**O**	o	o	△	o			
+6				**O**	o	o				
+7					**O**					

O : most common

Coordination Numbers and Structures

CN = 1,2, and 3

CN = 1, Rare



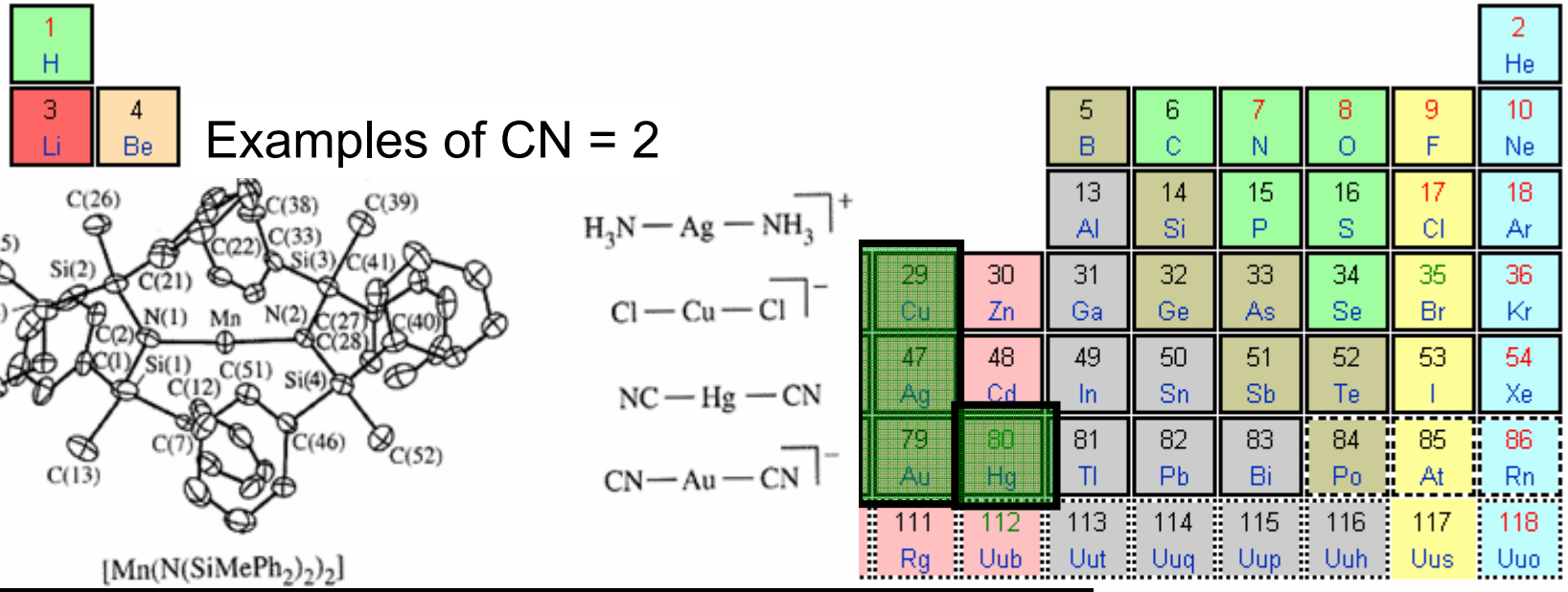
1 H														2 He
3 Li	4 Be									5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na										13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K										30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb										48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs										80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr										112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

* Lanthanides	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
** Actinides	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

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



Examples of CN = 2

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

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

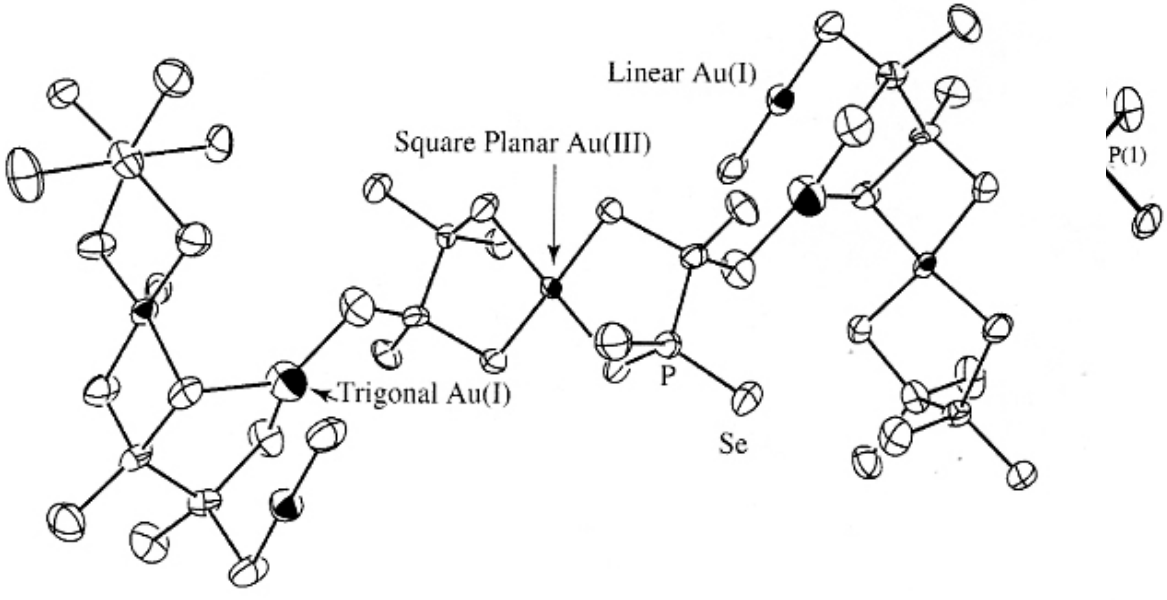


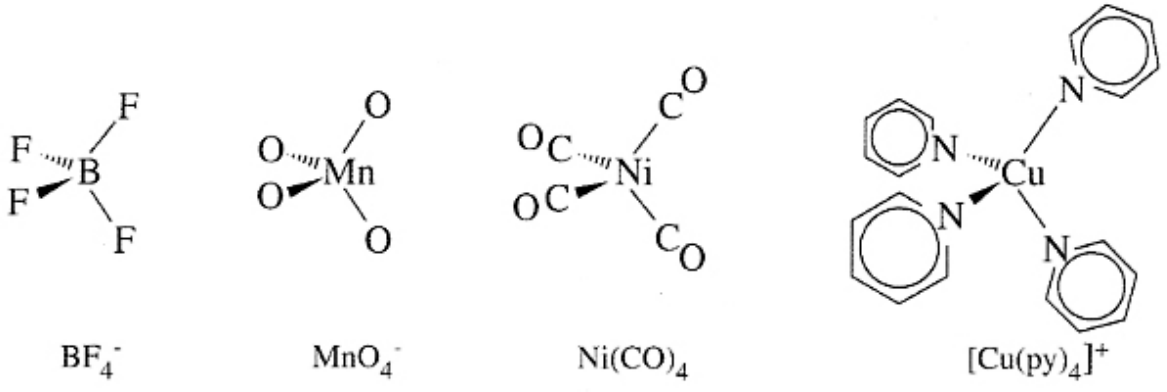
그림 9-24 $K_2Au_2P_2Se_6$. 세 가지 서로 다른 구조를 가지는 Au을 포함하는 화합물. 검은색 표시된 구, Au; 큰 무색 구, Se; 작은 무색 구, P. $[P_2Se_6]^{4-}$ 이온이 Au(I) 이온을 선형과 삼각형 구조로 연결하고 Au(III) 이온을 평면사각형 구조로 연결한다. 이 구조는 긴 사슬 모양을 하면서 K^+ 이온을 포함하는 긴 채널(channel)을 이루면서 적층되며 결정을 이룬다.
(K. Chordroudis, T. J. McCarthy, 그리고 M. G. Kanatzidis의 *Inorg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

1973, 12, 1170에서 발췌함).

Coordination Numbers and Structures

CN = 4

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



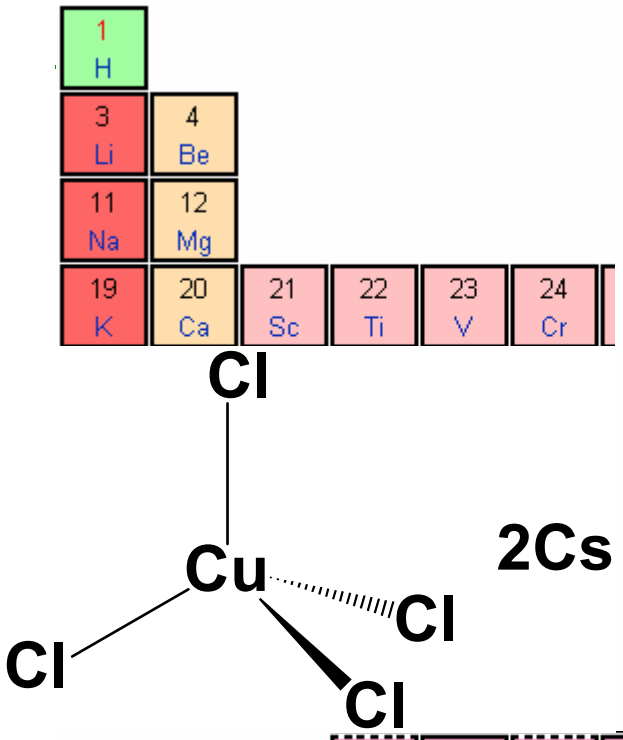
BF_4^- MnO_4^- $Ni(CO)_4$ $[Cu(py)_4]^+$

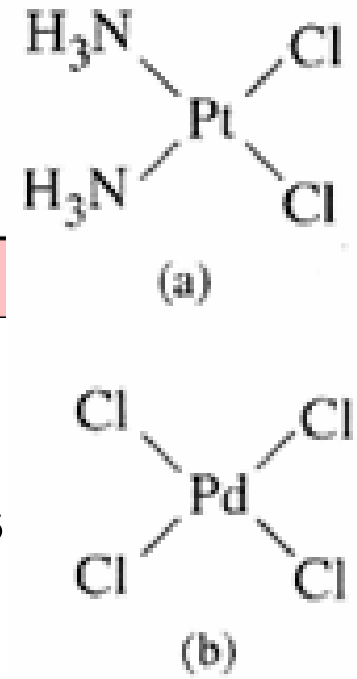
그림 9-25 정사면체 구조를 가지는 착화합물들.

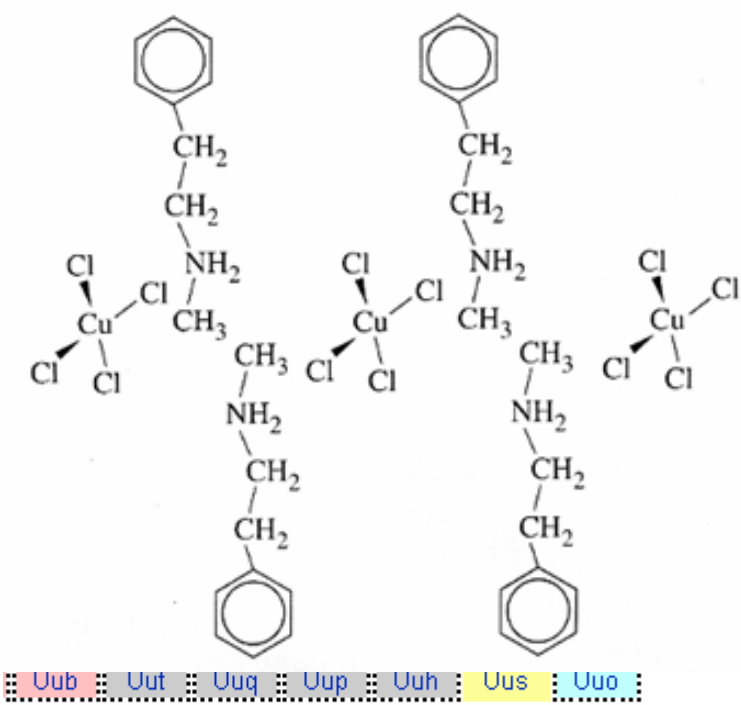
Coordination Numbers and Structures

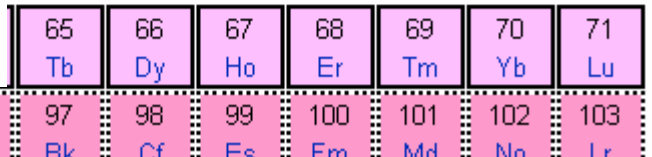
CN = 4

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))









Coordination Numbers and Structures

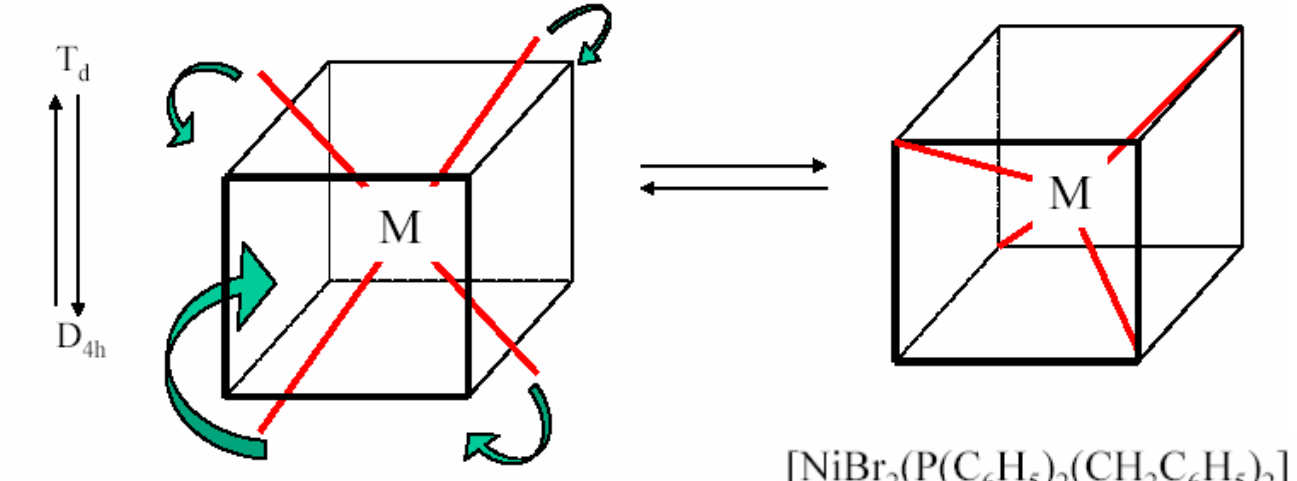
CN = 4

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



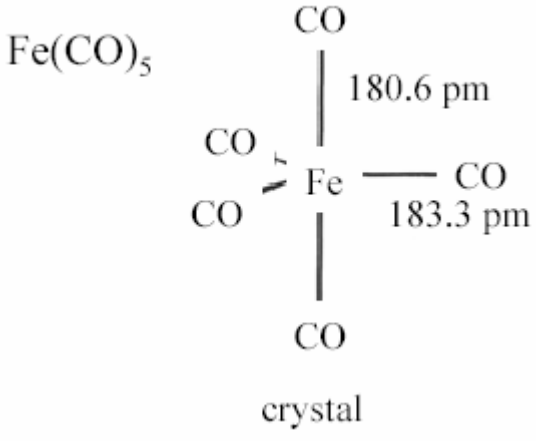
ΔE is not big.

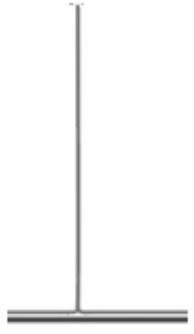
$[NiBr_2(P(C_6H_5)_2(CH_2C_6H_5)_2]$: both T_d and D_{4h} in the same crystal

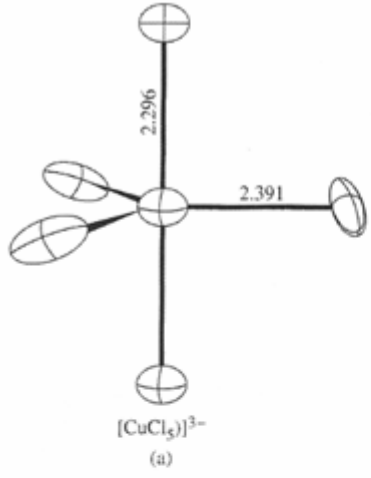
Coordination Numbers and Structures

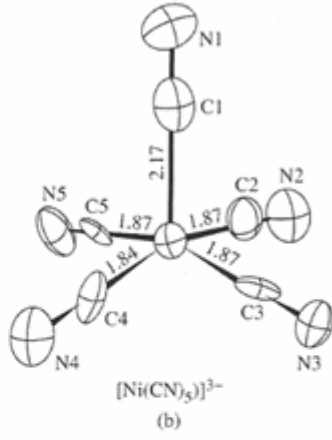
CN = 5

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

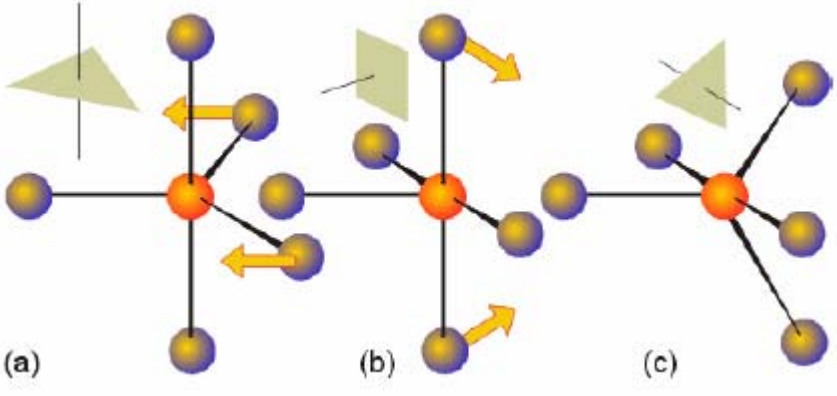




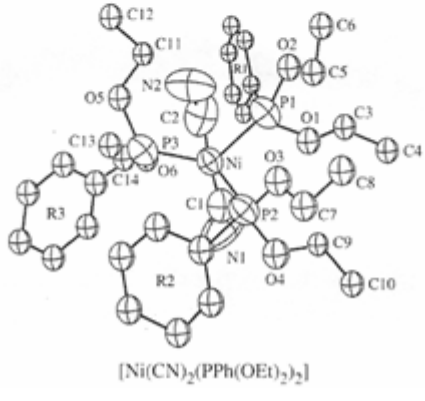




Fluxional behavior.



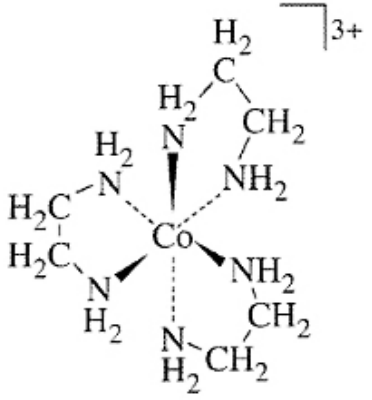
ΔE
C_{4v}



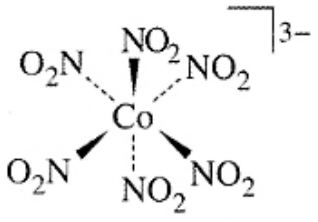
Coordination Numbers and Structures

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.

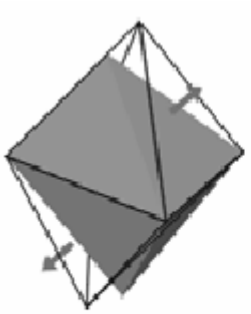
그림 9-29 정팔면체의 사각형 일그러짐.

O_h to D_{4h}

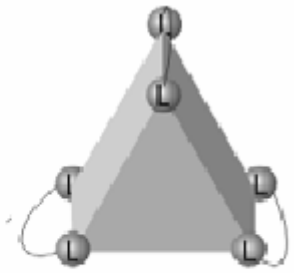
Coordination Numbers and Structures

CN = 6

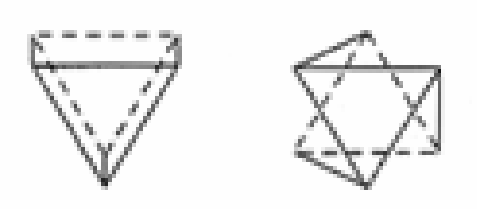
CN = 6, Octahedral (O_h) to Trigonal Prism (D_{3h})



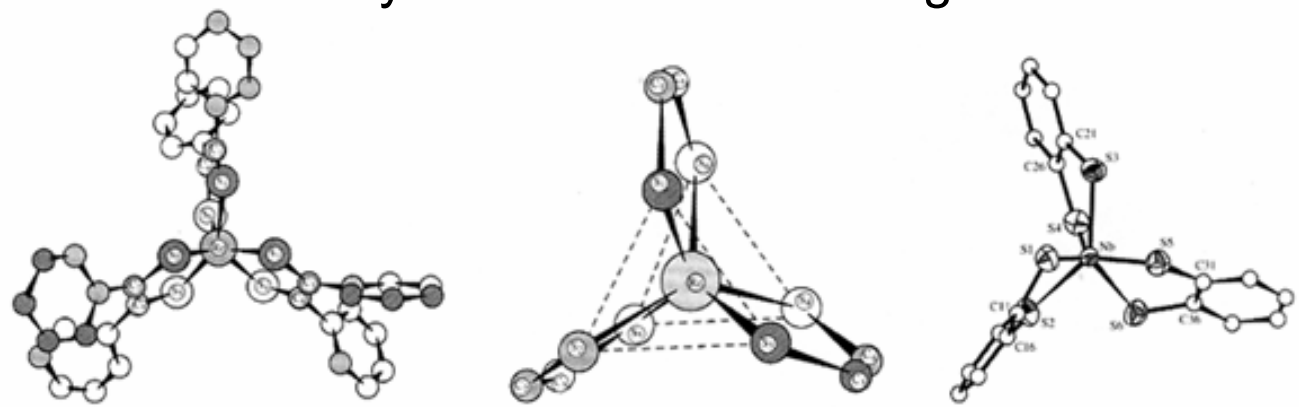
trigonal elongation
: trigonal antiprism (D_{3d})



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



Usually with three bidentate ligands

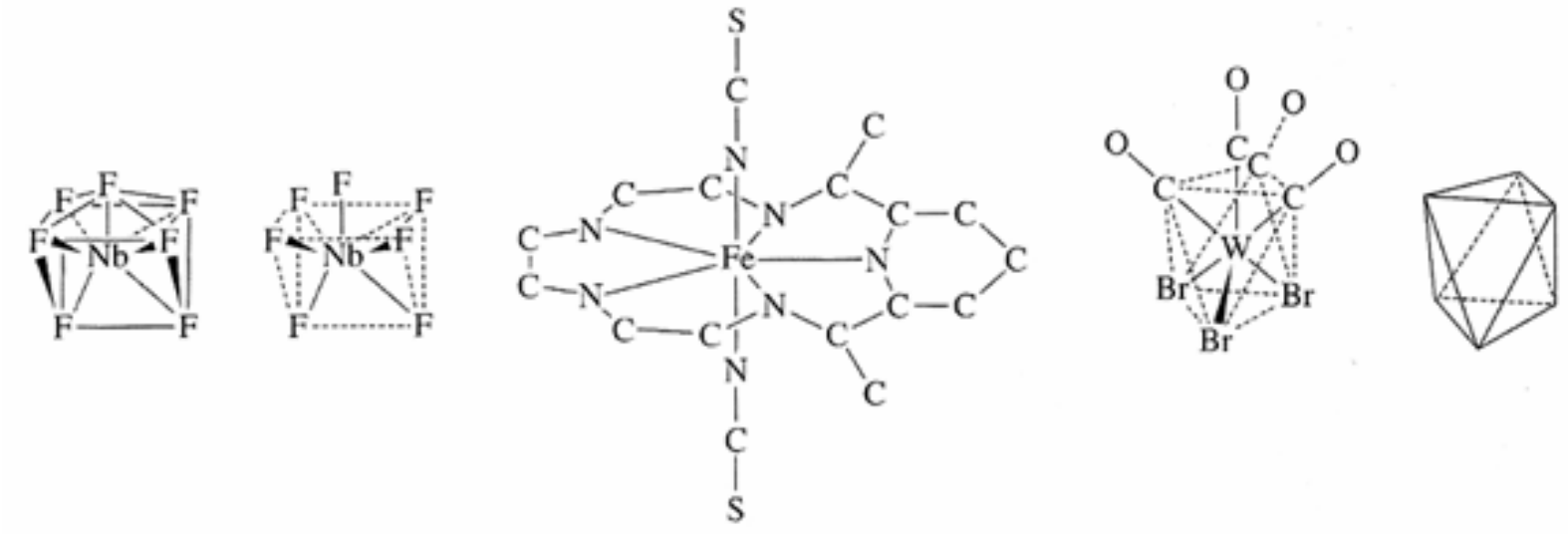


π Interactions between adiacent sulfur atoms

Coordination Numbers and Structures

CN = 7

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



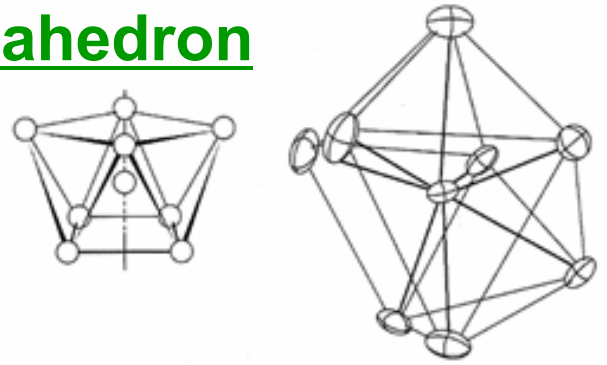
Capped trigonal prism Pentagonal bipyramid Capped octahedron

Different counterion, steric requirment

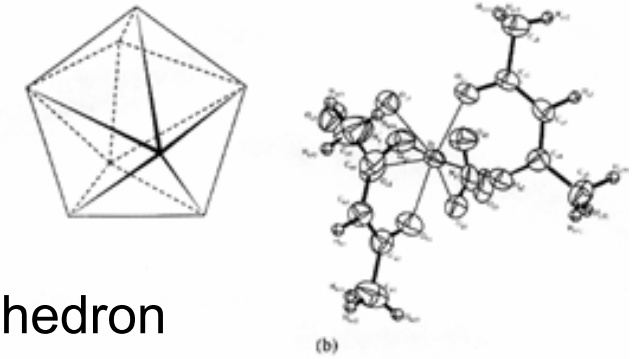
Coordination Numbers and Structures

CN = 8

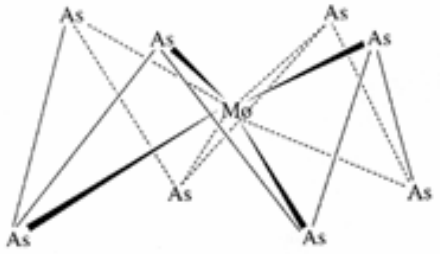
CN = 8, Square antiprism, Dodecahedron



Square antiprism



Dodecahedron



Compressed Square antiprism

Eight coordination is rare in the first row transition metals

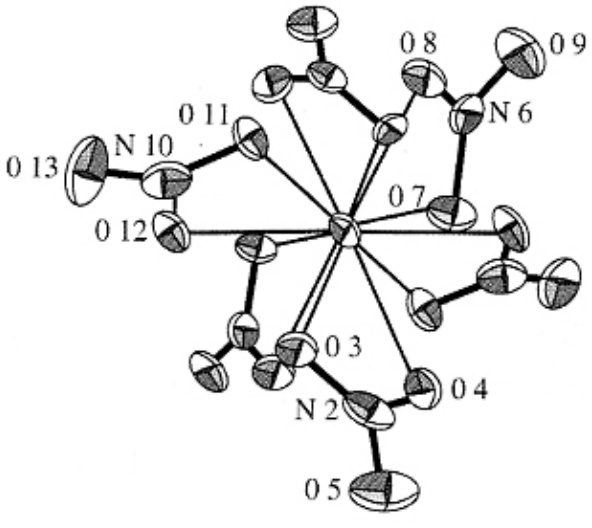
Why?

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

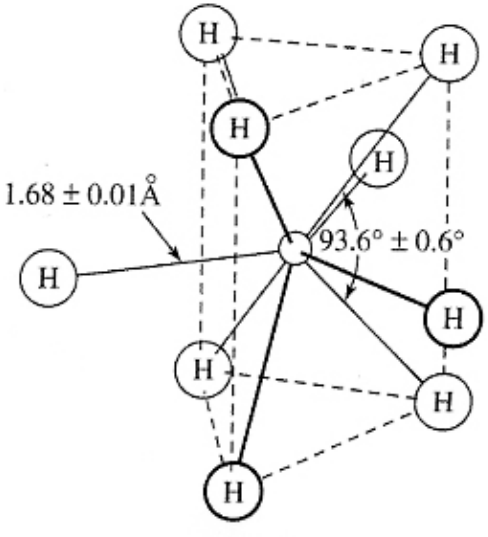
Coordination Numbers and Structures

CN ≥ 8

CN ≥ 8, known up to 16, not common



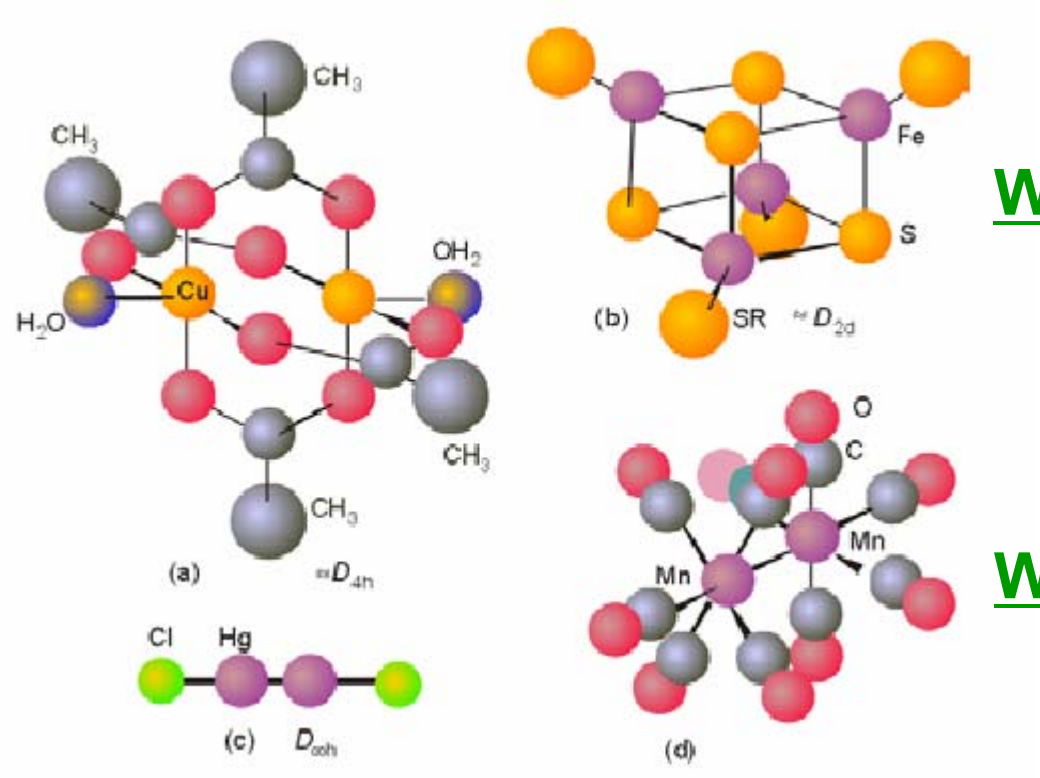
(a)



(b)

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-M bond