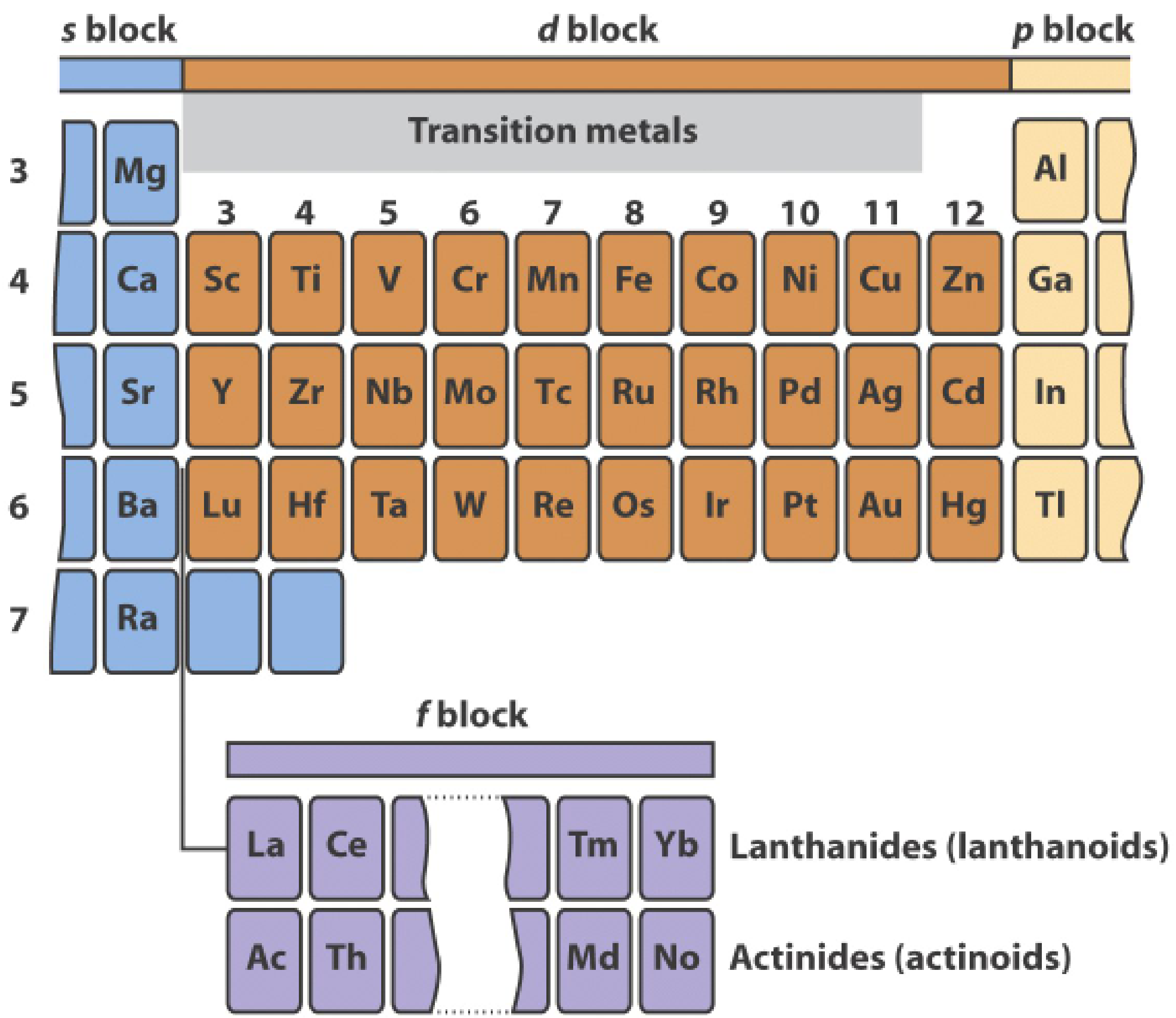
COORDINATION COMPLEXES

Prof.Dr. Amer A. Taqa

The d block metal form ***coordination complexes*** with molecules and ions



Transition Metal: Electronic Configurations

In the gas phase, ground state configuration of d-block elements:

$$[\text{Rare gas}]\ s^2\, d^{n-2}$$

In neutral metal complexes: d^n

In first row complexes, the 3d level is filled BEFORE the 4s.

Oxidation States and d-Occupancy

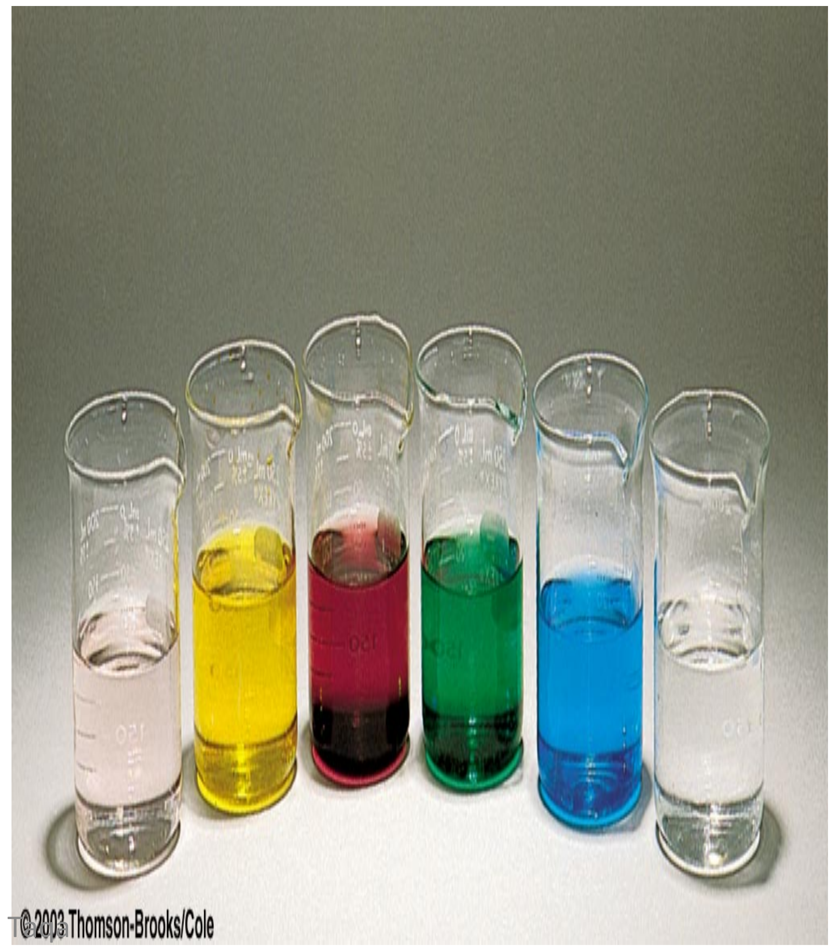
- **Oxidation state: No. electrons formally added/subtracted from neutral metal.**
- **Electrons are added/removed successively from the d-orbitals.**
- **d-occupancy is very important in understanding the chemistry of a metal complex.**

d-occupancy = group number – oxidation state

Complex	Oxidation State	Group number	d^n
$[NiCl_4]^{2-}$	+II	10	8
$[Ni(CO)_4]$	0	10	10
$[MnCl_4]^{2-}$	+II	7	5
$[Fe(OH_2)_6]^{3+}$	+III	8	5
$[V(CO)_6]^{-}$	-I	5	6

19.1 Coordination complexes

What is the electronic basis of the color of metal complexes?



Color and Magnetism

Colors of Period 4 Transition Metals

- e^- in partially filled d sublevel absorbs visible light
- moves to slightly higher energy d orbital

Magnetic properties due to unpaired electrons

Period 4 Transition Metals

Titanium, Ti   Chromium, Cr

Scandium, Sc   Vanadium, V   Manganese, Mn

Cobalt, Co   Copper, Cu

Iron, Fe   Nickel, Ni   Zinc, Zn

Determining oxidation states

"Difference between the number of valence electrons present in the zero oxidation state (neutral metal atom) and the number of valence electrons present in the metal after removal of the ligands in their closed shell states."

$[Cr(NH_3)_6]^{3+}$, $[MnO_4]^-$, $[Mn(CO)_4]^{3-}$, $[CoCl_2(en)_2]^+$

Determine the oxidation states and d-occupancy of the metal ion in these complexes

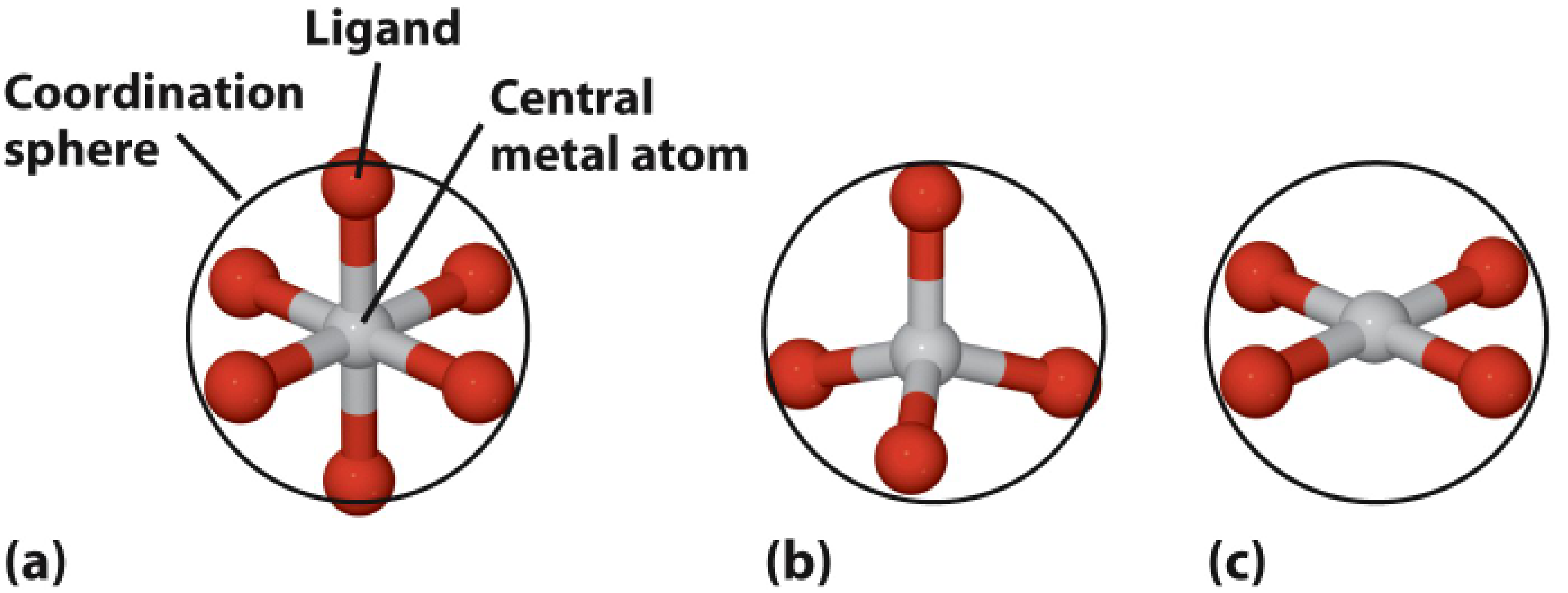
Coordination complex: A structure containing a **metal** (usually a metal ion) bonded (coordinated) to a group of surrounding **molecules or ions**.

Ligand (ligare is Latin, to bind): A ligand is a molecule or ion that is directly bonded to a metal ion in a coordination complex

A ligand uses a **lone pair of electrons** (Lewis base) to bond to the metal ion (Lewis acid)

Coordination sphere: A metal and its surrounding ligands

Complex ions: Three common structural types



Octahedral:
Most important

Tetrahedral

Square planar

What determines why a metal takes one of these shapes?

Lewis acids and bases

A Lewis base is a molecule or ion that donates a lone pair of electrons to make a bond

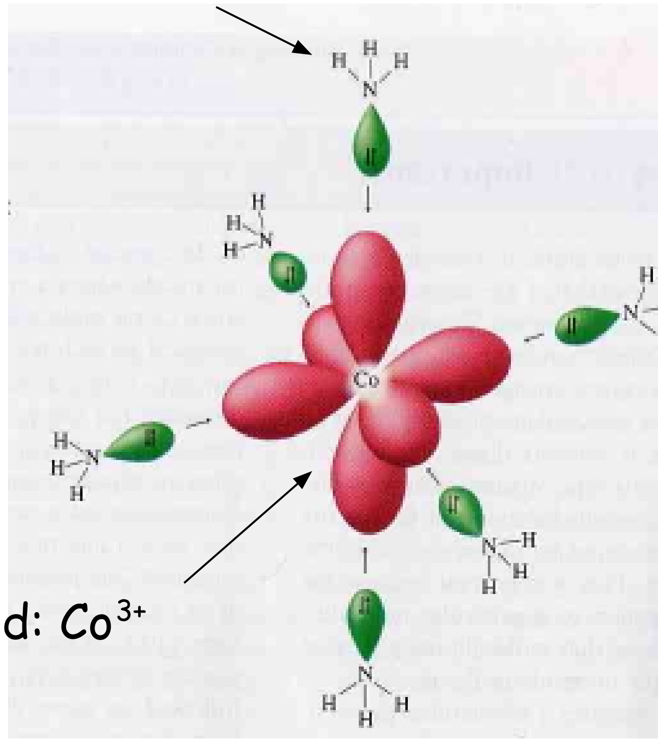
Examples: $:NH_3$ $:OH_2$ $:Cl^-$ $:F^-$

A Lewis acid is a molecule of ion that accepts a lone pair of electrons to make a bond

Examples: H^+ Co^{3+} Co^{2+} M^{n+}

The formation of a coordinate complex is a ***Lewis acid-base*** reaction

Lewis base: $:NH_3$



Lewis acid: Co^{3+}

Coordination complex: Lewis base (electron pair donor) coordinated to a Lewis acid (electron pair acceptor)

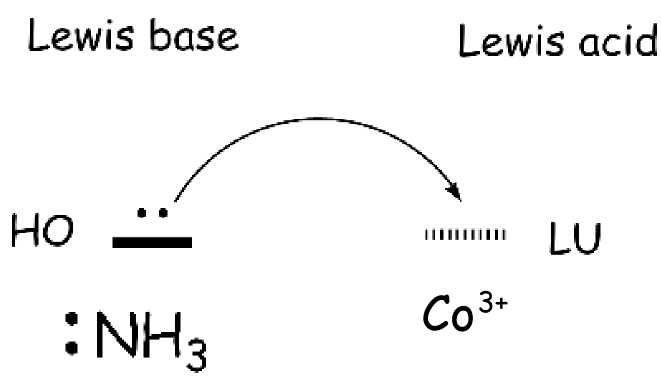
Coordination complex: Ligand (electron donor) coordinated to a metal (electron acceptor)

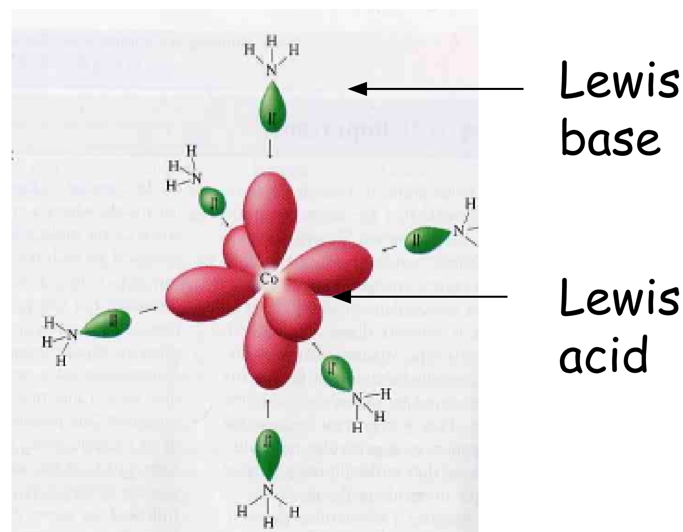
The number of ligand bonds to the central metal atom is termed the coordination number

The basic idea is that the ligand (Lewis base) is providing electron density to the metal (Lewis acid)

The bond from ligand to metal is covalent (shared pair), but both electrons come from the ligand (coordinate covalent bond)

In terms of theory we visualize the coordination as the transfer of electrons from the orbital of the Lewis base to the lowest unoccupied orbital of the Lewis acid





Types of Ligands (electron pair donors: ***Monodentate*** (one tooth) Ligands

Latin: "mono" meaning one and "dens" meaning tooth

TABLE 19–1 Common Monodentate Ligands and Their Names

Ligand	Formula	Name
Fluoride ion	$:F^-$	Fluoro
Chloride ion	$:Cl^-$	Chloro
Nitrite ion	$:NO_2^-$	Nitro
	$:ONO^-$	Nitrito
Carbonate ion	$:OCO_2^{2-}$	Carbonato
Cyanide ion	$:CN^-$	Cyano
Thiocyanate ion	$:SCN^-$	Thiocyanato
	$:NCS^-$	Isothiocyanato
Hydride ion	$:H^-$	Hydrido
Oxide ion	$:O^{2-}$	Oxido
Hydroxide ion	$:OH^-$	Hydroxo
Water	$:OH_2$	Aqua
Ammonia	$:NH_3$	Ammine
Carbon monoxide	$:CO$	Carbonyl
Nitrogen monoxide	$:NO$	Nitrosyl

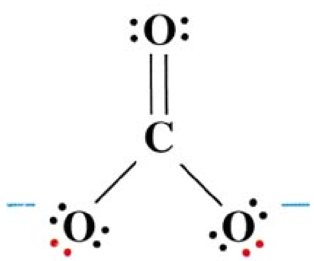
The ligating atom is indicated by a pair of red dots representing a lone pair of electrons. In the CO_3^{2-} ligand, either one or two of the oxygen atoms can donate a lone pair to the metal.

Anions

Molecules with lone pairs

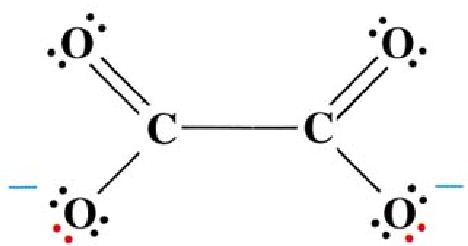
Types of Ligands: Bidentate (two tooth) Ligands

Some common bidentate (chelates):



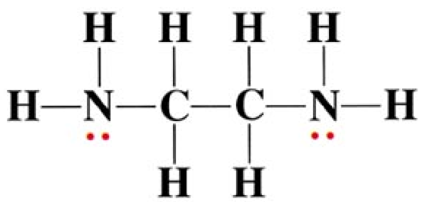
Carbonate ion,
CO_3^{2-}

(a)



Oxalate ion,
$C_2O_4^{2-}$

(b)

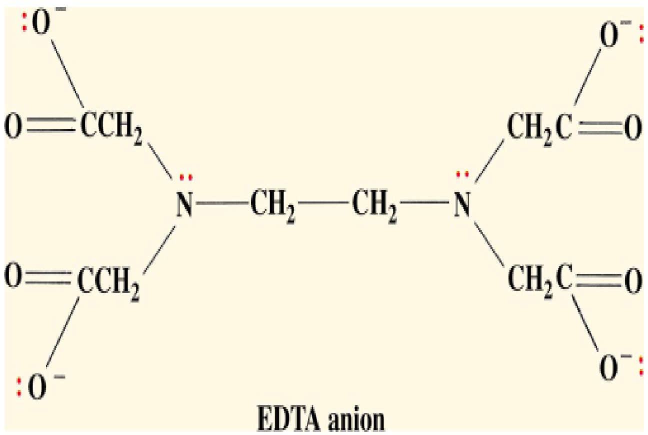


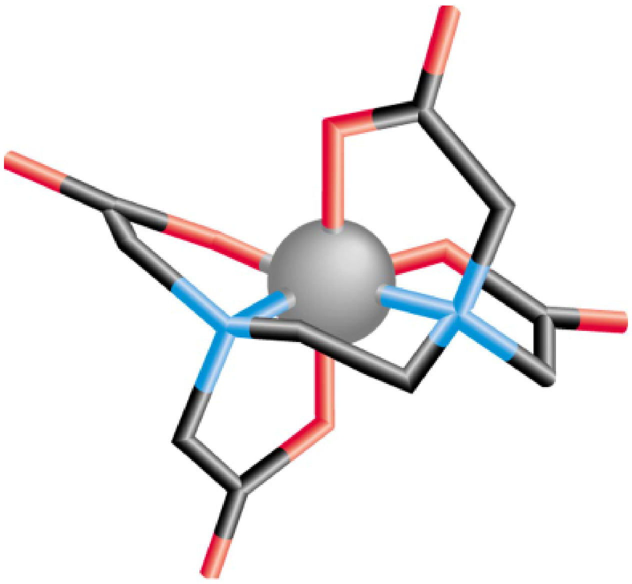
Ethylenediamine,
$NH_2CH_2CH_2NH_2$ (en)

(c)

Types of Ligands: Ethylenediaminetetraacetate ion (EDTA): a polydentate ***chelating*** ligand

Chelate from
Greek *chela*, "claw"





EDTA wraps around the metal ion at all 6 coordination sites producing an exceedingly tight binding to the metal

Alfred Werner
Switzerland
University of Zurich
Zurich, Switzerland
b. 1866
(in Mulhouse, then Germany)
d. 1919

Alfred Werner: the father of the structure of coordination complexes

The Nobel Prize in Chemistry 1913
"in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry"

Alfred Werner – Founder of Coordination Chemistry

"Dot" Representation:

Pentachlorophosphorous PCl_5
$PCl_3 \cdot Cl_2$

Copper(II) Sulfate Pentahydrate
$CuSO_4 \cdot 5H_2O$

Copper(II) Acetate Hydrate
$Cu(CH_3COO)_2 \cdot H_2O$

Hex(a)ammin Cobalt(III) Chloride
$CoCl_3 \cdot 6NH_3$

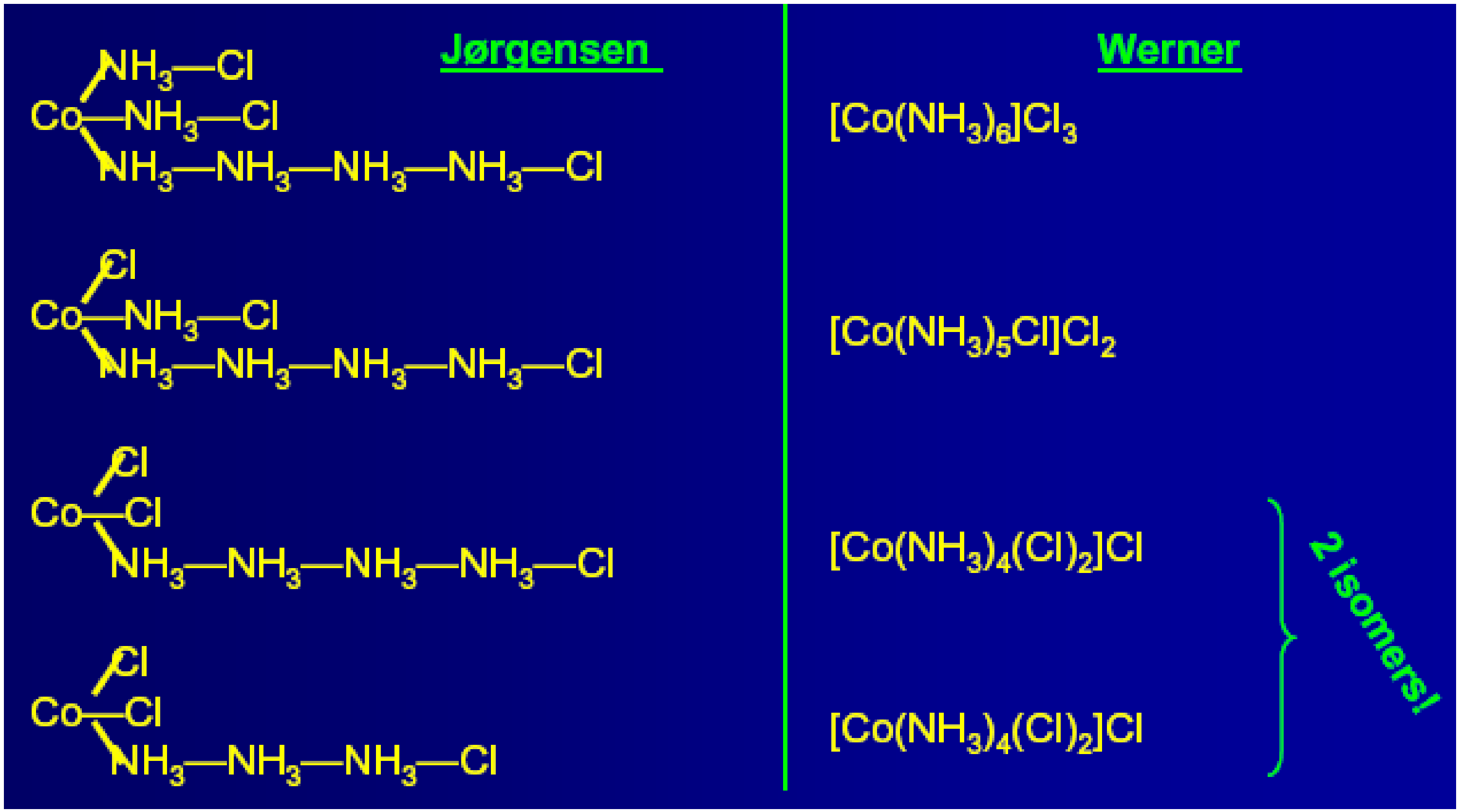
Werner's complexes

Reaction of $CoCl_3$ with NH_3:

Early Form	Present Form	Colour	Early Name
$CoCl_3.6NH_3$	$[Co(NH_3)_6]Cl_3$	yellow	*luteo* complex
$CoCl_3.5NH_3$	$[Co(NH_3)_5Cl]Cl_2$	purple	*purpureo* complex
$CoCl_3.4NH_3$	$[Co(NH_3)_4Cl_2]Cl$	violet (*cis*)	*violeo* complex
		green (*trans*)	*praseo* complex

Hex(a)ammin Cobalt(III) Chloride
$CoCl_3 \cdot 6NH_3$

Prefix	Color	Complex
luteo	yellow	$Co^{III}Cl_3 \cdot 6NH_3$
purpureo	red	$Co^{III}Cl_3 \cdot 5NH_3$
praseo	green	$Co^{III}Cl_3 \cdot 4NH_3$
violeo	violet	$Co^{III}Cl_3 \cdot 4NH_3$


Jørgensen
Werner
[Co(NH3)6]Cl3
[Co(NH3)5Cl]Cl2
[Co(NH3)4(Cl)2]Cl
[Co(NH3)4(Cl)2]Cl
2 isomers!

(1) A coordination compounds is a ***neutral*** species consisting of a coordinate complex and uncoordinated ions required to maintain the charge balance

(2) Brackets [] are used to indicate all of the atomic composition of the coordinate complex: the central metal atom and the ligands. The symbol for the central metal atom of the complex is first within the brackets

(3) Species outside of the [] are not coordinated to the metal but are require to maintain a charge balance

$[Co(NH_3)_6]^{3+}$ ← $[Co(NH_3)_6]Cl_3$ → $3\ Cl^-$

Composition of complex

Free species

Werner's explanation of coordination complexes

Metal ions exhibit two kinds of valence: primary and secondary valences

The primary valence is the oxidation number (positive charge) of the metal (usually 2+ or 3+)

The secondary valence is the number of atoms that are directly bonded (coordinated) to the metal

The secondary valence is also termed the "coordination number" of the metal in a coordination complex

Exemplar of primary and secondary valence: $[Co(NH_3)_6]Cl_3$

What is the atomic composition of the complex?

$[Co(NH_3)_6]Cl_3$

What is the net charge of the complex?

$[Co(NH_3)_6]^{3+}$

How do we know the charge is 3+ on the metal?

3+ is required to balance the three Cl^- ions

The primary valence of $[Co(NH_3)_6]Cl_3$ is 3 (charge on Co^{3+})

The secondary valence of $[Co(NH_3)_6]Cl_3$ is 6 (six ligands)

Structures of Coordination Complexes: The ammonia complexes of Co(III) = Co^{3+}

How did Werner deduce the structure of coordination complexes?

Composition	Ions released	Color
$CoCl_3 \cdot 6NH_3$	3 "free" Cl^- ions	Orange-Yellow
$CoCl_3 \cdot 5NH_3$	2 "free" Cl^- ions	Purple
$CoCl_3 \cdot 4NH_3$	1 "free" Cl^- ions	Green
$CoCl_3 \cdot 3NH_3$	0 "free" Cl^- ions	Green

In all of these complexes there are no free NH_3 molecules
(No reaction with acid)

"free" Cl^- is not in sphere; all NH_3 molecules are is in sphere

Compound 1: $CoCl_3{\cdot}6NH_3$ = $[Co(NH_3)_6]^{3+}(Cl^-)_3$ = $[Co(NH_3)_6](Cl)_3$

Conclude: 3 free Cl^- ions, ***complex = $[Co(NH_3)_6]^{3+}$***

Compound 2: $CoCl_3{\cdot}5NH_3$ = $[Co(NH_3)_5Cl]^{2+}(Cl^-)_2$ = $[Co(NH_3)_5Cl](Cl)_2$

Conclude: 2 free Cl^- ions, ***complex = $[Co(NH_3)_5Cl]^{2+}$***

Compound 3: $CoCl_3{\cdot}4NH_3$ = $[Co(NH_3)_4Cl_2]^{1+}(Cl^-)$ = $[Co(NH_3)_4Cl_2](Cl)$

Conclude: 1 free Cl^- ion, ***complex = $[Co(NH_3)_4Cl_2]^{1+}$***

Compound 4: $CoCl_3{\cdot}3NH_3$ = ***$[Co(NH_3)_3Cl_3]$ = complex***

No free Cl^- ions, both Cl^- and NH_3 in sphere

Difference in reactivity

$CoCl_3.6NH_3$ + excess Ag^+ ⟶ 3 AgCl (ppt)

$CoCl_3.5NH_3$ + excess Ag^+ ⟶ 2 AgCl (ppt)

$CoCl_3.4NH_3$ + excess Ag^+ ⟶ 1 AgCl (ppt)

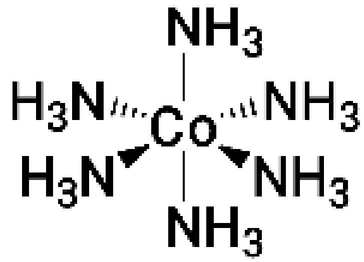
(*praseo* or *violeo*)

Postulate:

- Cobalt has a constant coordination number of 6
- As NH_3 are removed, they are replaced by Cl^- ions that became covalently bound to cobalt

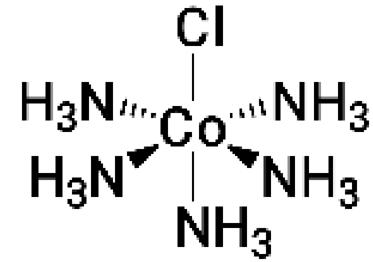
Coordination complexes: Three dimensional structures

$CoCl_3 \cdot 6NH_3$



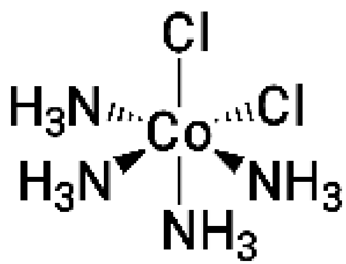
Cl^- Cl^- Cl^-

$CoCl_3 \cdot 5NH_3$

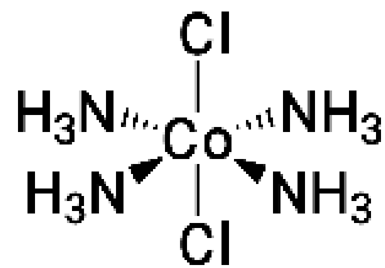


Cl^- Cl^-

$CoCl_3 \cdot 4NH_3$

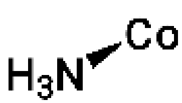


Cl^-



Cl^-

Isomers!



Bond toward you

Bond away from you

Coordination numbers and geometries

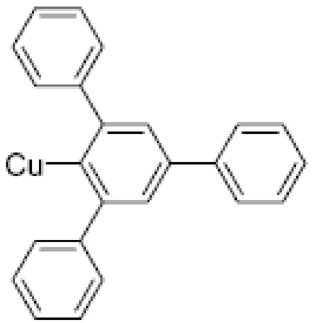
CN	Common geometries	Less common geometries
2	Linear	
3	Trigonal planar	Trigonal pyramidal
4	Tetrahedral; square planar	
5	Trigonal bipyramidal; square-based pyramidal	
6	Octahedral	Trigonal prismatic
7	Pentagonal bipyramidal	Monocapped trigonal prismatic; monocapped octahedral
8	Dodecahedral; square antiprismatic; hexagonal bipyramidal	Cube; bicapped trigonal prismatic
9	Tricapped trigonal prismatic	

(a) Low coordination numbers: 2, 3

Coordination 2: Limited to Group 11 metals with +1 oxidation state (d^{10}):

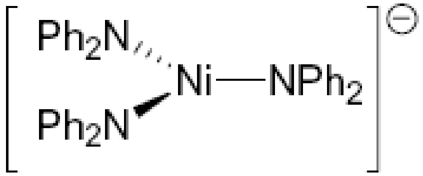
$[AuCl(PEt_3)]$, $[CuCl_2]^-$, $[AgCl_2]^-$, $[Au(CN)_2]^-$, $[Hg(CN)_2]$ and $[HgMe_2]$ **(all linear)**

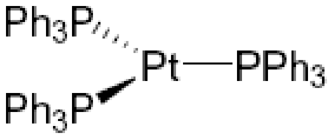
Or sterically bulky ligands:



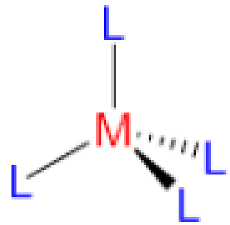
$[Cu(C_6H_2Ph_3\text{-}2,4,6)]$

Coordination 3: Not common





(b) Four Coordination



Tetrahedral

Favoured over higher CN's if the central atom is small or the ligands are large (Cl^-, Br^-, I^-). Common for oxoanions of metal atoms in high oxidation states and for halide complexes of M^{2+} in the first row of the d-block.

d^0: $[VO_4]^{3-}$, $[CrO_4]^{2-}$, $[MoS_4]^{2-}$, $[WS_4]^{2-}$, $[MnO_4]^-$, $[TcO_4]^-$, RuO_4, OsO_4
d^1: $[MnO_4]^{2-}$, $[TcO_4]^{2-}$, $[ReO_4]^{2-}$, $[RuO_4]^-$
d^2: $[FeO_4]^{2-}$, $[RuO_4]^{2-}$
d^5: $[FeCl_4]^-$, $[MnCl_4]^{2-}$
d^6: $[FeCl_4]^{2-}$, $[FeI_4]^{2-}$
d^7: $[CoCl_4]^{2-}$
d^8: $[NiCl_4]^{2-}$, $[NiBr_4]^{2-}$
d^9: $[CuCl_4]^{2-}$ (distorted)
d^{10}: $[ZnCl_4]^{2-}$, $[HgBr_4]^{2-}$, $[CdCl_4]^{2-}$, $[Zn(OH)_4]^{2-}$, $[Cu(CN)_4]^{3-}$, $[Ni(CO_4)]$.

Square planar:

- Rarer than tetrahedral
- Associated with d^8 metal ions Rh^+, Ir^+, Pd^{2+}, Pt^{2+} and Au^{3+}

e.g. $[PdCl_4]^{2-}$, $[PtCl_4]^{2-}$, $[AuCl_4]^-$, $[AuBr_4]^-$, $[RhCl(PPh_3)_3]$

(c) Five Coordination

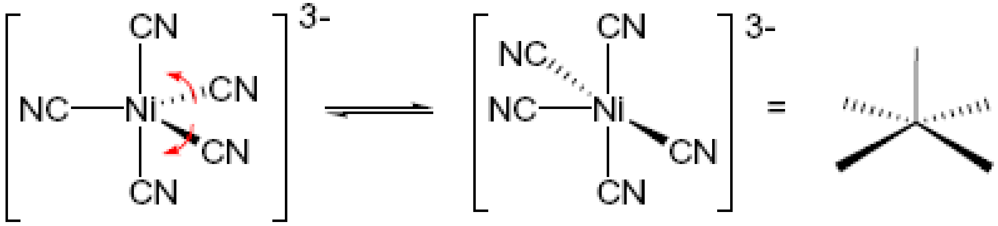
Trigonal bipyrimidal:

$[CdCl_5]^{3-}$, $[HgCl_5]^{3-}$ and $[CuCl_5]^{3-}$ (d^{10})

Square Pyramidal:

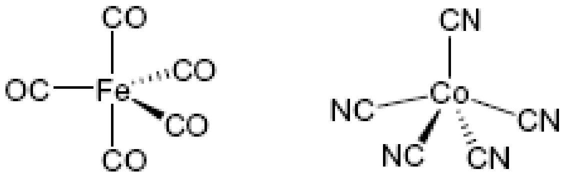
$[NbCl_4(O)]^-$ (d^0); $[V(acac)_2(O)]$ (d^1), $[TcCl_4(N)]^-$ (d^1), $[ReCl_4(O)]^-$ (d^2)

Small energy difference between trigonal bipyramidal and square pyramidal



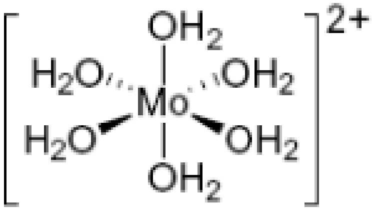
Barry pseudo-rotation

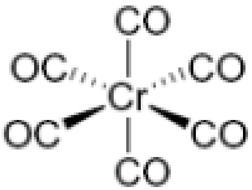
Common for the ligands to physically exchange between these sites (‘*fluxionality*’)

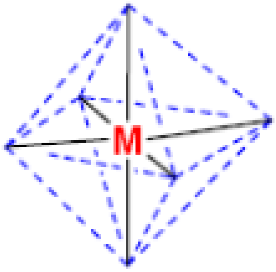


(d) Six coordination

The octahedral geometry is the most important among the d^1 to d^9 complexes

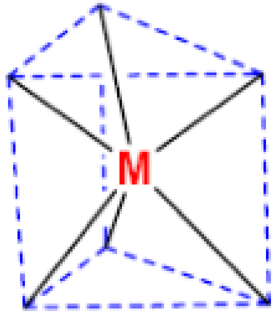


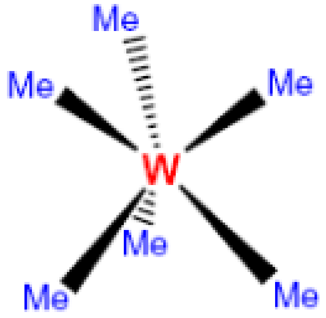




Distortions for MX_5Y, MX_4Y_2 and MX_3Y_3 complexes (*e.g.* Jahn-Teller) are very common (see later).

There are few examples of trigonal prismatic structures, *e.g.* d^0 complexes of ML_6, WMe_6:





Transition metal coordination compounds: Features

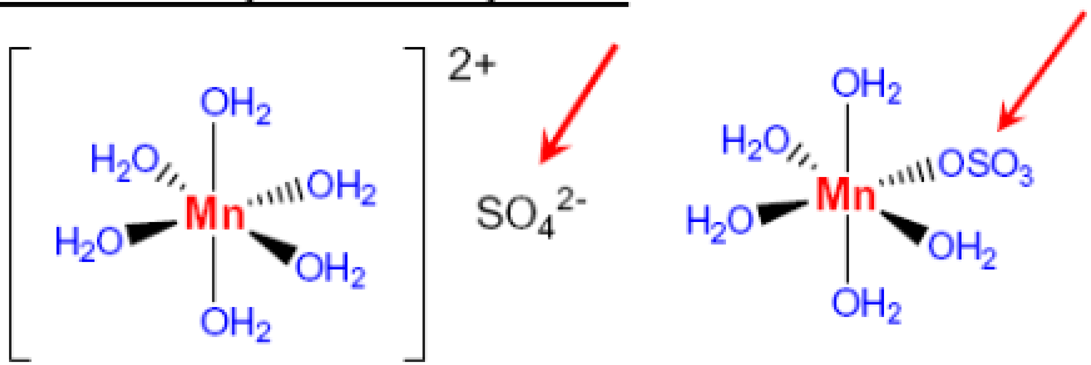
1. Type of Complex

Neutral: $[RhCl_2(OH_2)_3]$

Anionic: $Na_4^+[Fe(CN)_6]^{4-}$

Cationic: $[Co(NH_3)_6]^{2+}\ Cl^{2-}$

2. Inner/Outer Sphere Complexes



Outer: ligands bound electrostatically without displacing bound ligands.

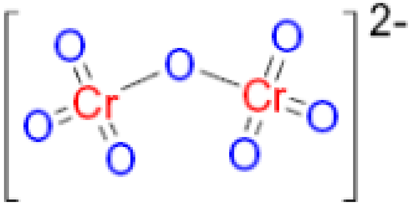
Inner: ligands directly bound to the metal centre (Primary coordination sphere)

3. Nuclearity

Mononuclear

Binuclear:

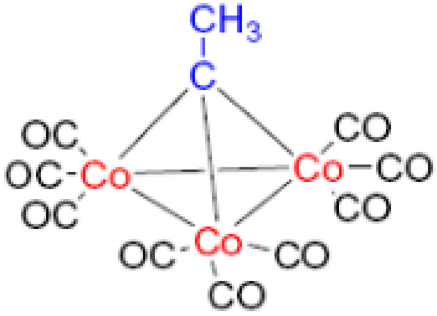
2 acceptors bridged by a ligand, *e.g.* dichromate



Polynuclear (Clusters):

Bridging ligand denoted by 'μ' + number of metals involved (2 usually omitted)

e.g. $[Co_3(\mu 3\text{-}C\text{-}CH_3)(CO)_9]$, a trinuclear, tribridged complex



Nomenclature

1. Sequence of central atom and ligand names

In formulae:

Ligands (first ionic, then neutral)

Charge(s)
In superscript

$$[M(L^1)_m(L^2)_n]^{p+}$$

Square
bracket

Central atom(s) first

In names:

Dichloro(diphenylphosphine)(thiourea)platinum(II)

Ligands (listed alphabetically, regardless of charge and numerical prefixes)

Central atom placed after ligands

Oxidation State in parenthesis

2. Number of ligands in a complex

Two types of numerical prefixes:
(i) Bis, tris, tetrakis, pentakis…

(ii) di, tri, tetra, penta, hexa, hepta…

(i) is recommended, but (ii) is also used for complicated ligands and when ambiguity may arise:
e.g. dichloro, diamine, bis(triphenylphosphine), bis(methylamine)

Dibromobis(trimethylphosphine)platinum(II)

3. Termination of name of complexes

Anionic complexes ends in 'ate'. None for cationic or neutral complexes

e.g. $[PtCl_4]^{2-}$ tetrachloroplatinate(II)

$[Fe(CO)_4]^{2-}$ tetracarbonylferrate(-II)

Metal	Name in anionic complex
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argenate
Gold	Aurate
Tin	Stannate

4. Oxidation numbers, charge numbers

Oxidation state number, where known, is indicated by a roman numeral; Charge numbers may be indicated by arabic numerals preceding the charge sign.

e.g. $K_4[Fe(CN)_6]$ Potassium hexacyanoferrate(II); or Potassium hexacyanoferrate(4-)

Name the following complexes:

$[PtCl(NH_2CH_3)(NH_3)_2]Cl$

$Na[PtBrCl(ONO)(NH_3)]$

$[Co(OH_2)_2(NH_3)_4]Cl_3$

Coordination Compound

- Consist of a complex ion and necessary counter ions
- $[Co(NH_3)_5Cl]Cl_2$
-
- Complex ion: $[Co(NH_3)_5Cl]^{2+}$
- $Co^{3+} + 5\ NH_3 + Cl^-$
- $= 1(3+) + 5\ (0) + 1(1-)$
- $= 2+$

- Counter ions: $2\ Cl^-$

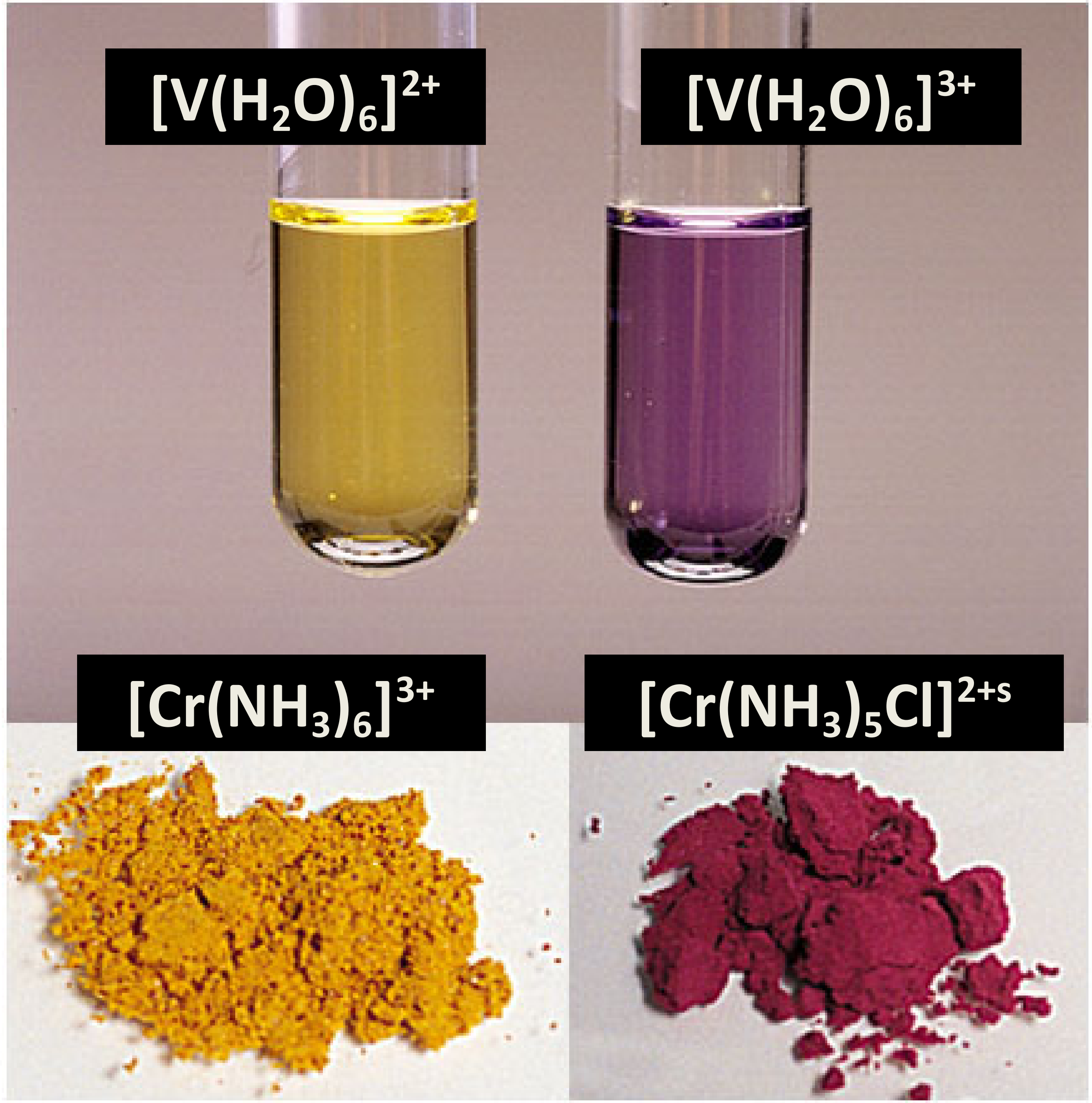
NOW some for you to try!!!

$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate(III)
$K_2[PtCl_4]$	Potassium tetrachloroplatinate(II)
$Na_2[Fe(CO)_4]$	Sodium Tetracarbonylferrate(II)
$[Co(H_2O)_2(NH_3)_4]Cl_3$	Tetraammindiaquacobalt(III) chloride
$[Ni(H_2O)(NH_3)_4]SO_4$	Tetraaminediaquanickel(II) sulfate
$Na_2[OsCl_5N]$	Sodium pentachloronitridoosmate(VI)
$[CoCl(NO_2)(NH_3)_4]Cl$	Tetraaminechloronitritocobalt(III) chloride
$[CoCl(NH_2)(en)_2]NO_3$	Amidochlorobis(ethylenediamine)cobalt(III) chloride
$[FeH(CO)_3(NO)]$	Tricarbonylhydridonitrosyliron(I) ?(II)??
$[PtCl(NH_2CH_3)(NH_3)]Cl$	Amminchloro(methylamine) platinum(II) chloride

Effects of Metal Oxidation State and of Ligand on Color

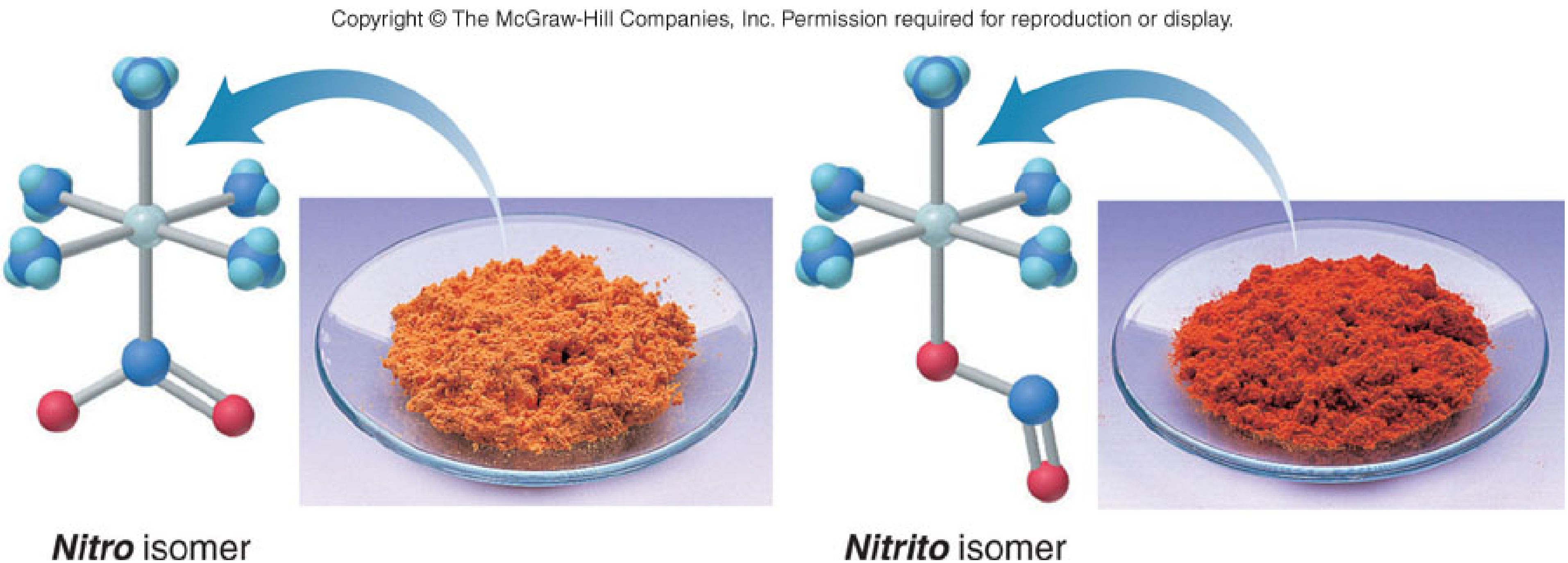
A

B



© McGraw-Hill Higher Education/Stephen Frisch, photographer

Linkage Isomers



$[Co(NH_3)_5(NO_2)]Cl_2$

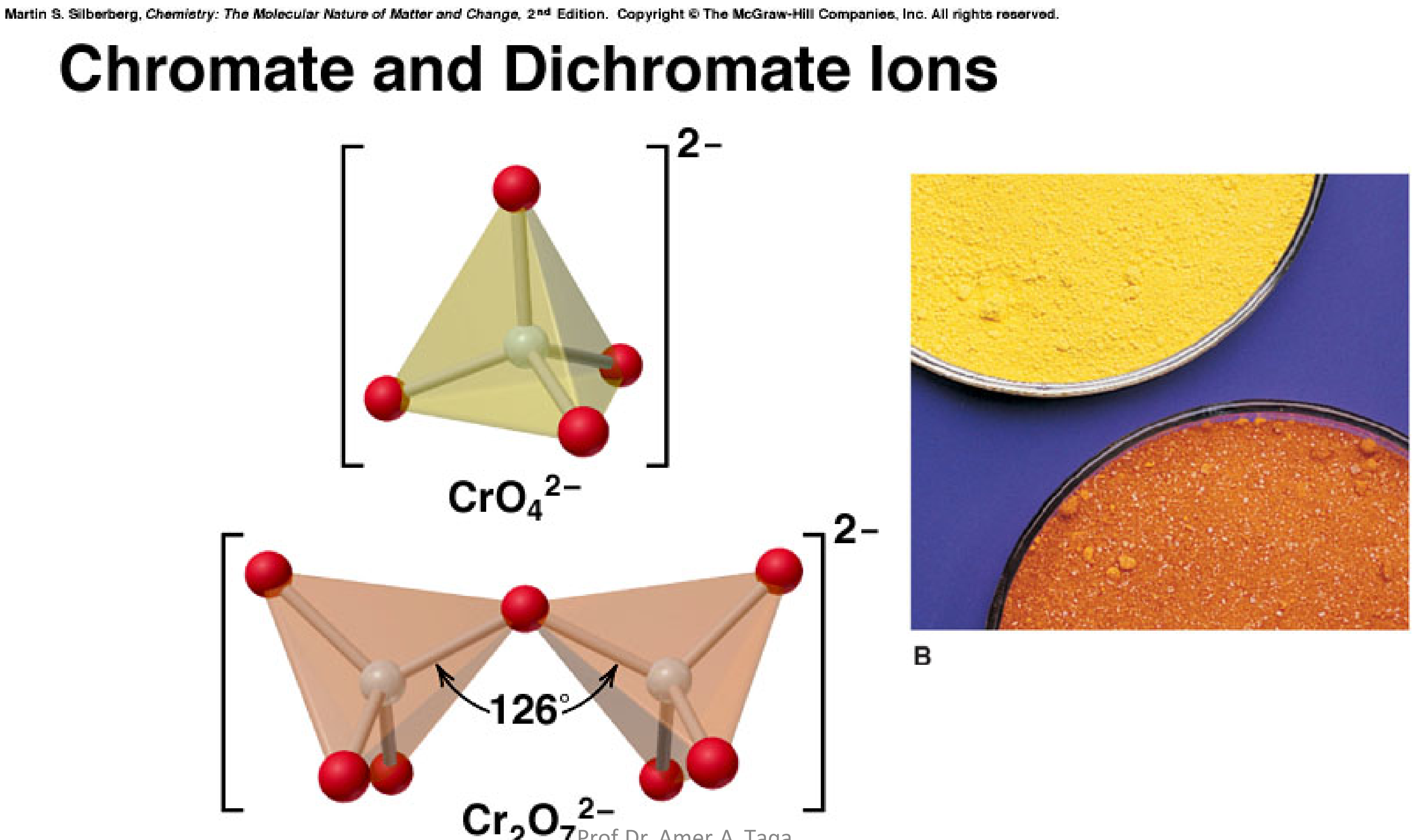
Pentaamminenitrocobalt(III) chloride

$[Co(NH_3)_5(ONO)]Cl_2$

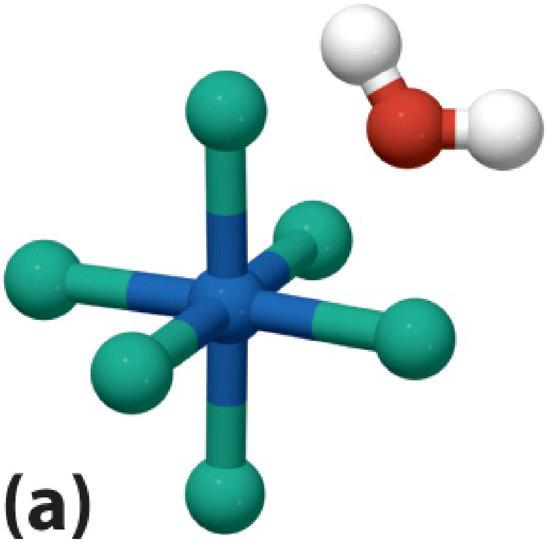
Pentaamminenitritocobalt(III) chloride

Chromium

Chemical properties reflect oxidation state

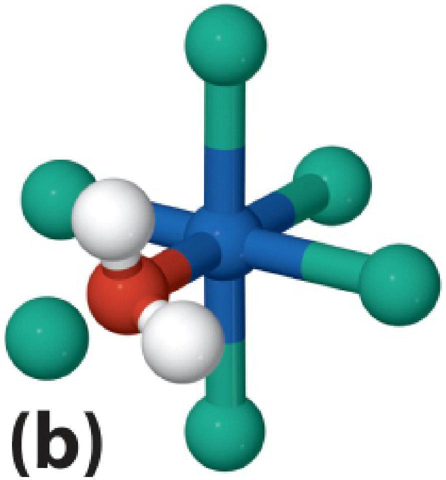


Hydrate isomers:



(a)

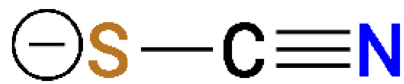
Water in outer sphere (water that is part of solvent)

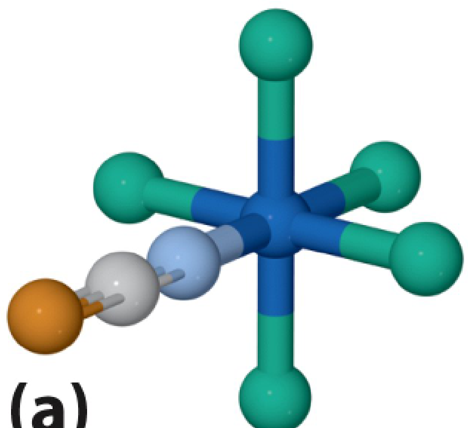


(b)

Water in the inner sphere water (water is a ligand in the coordination sphere of the metal)

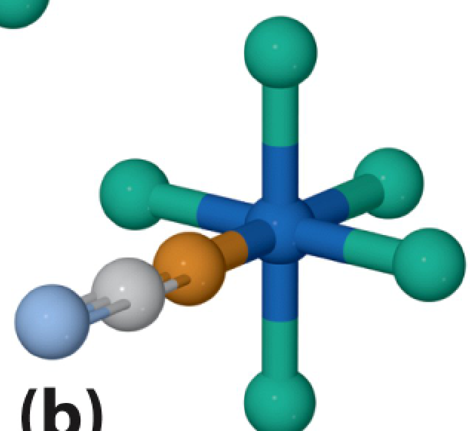
Linkage isomers

Example:  Bonding to metal may occur at the S or the N atom



(a)

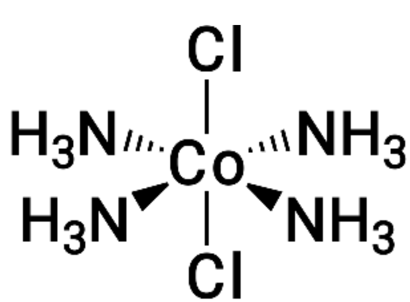
Bonding occurs from N atom to metal



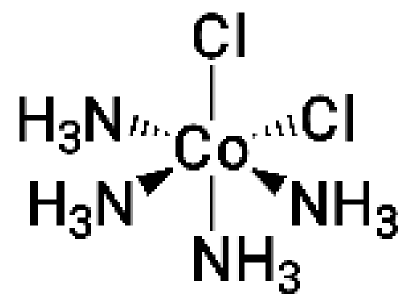
(b)

Bonding occurs from S atom to metal

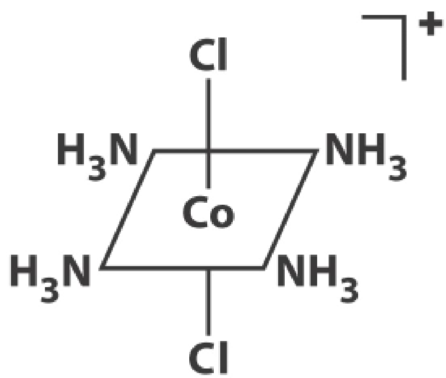
Stereoisomers: geometric isomers (cis and trans)



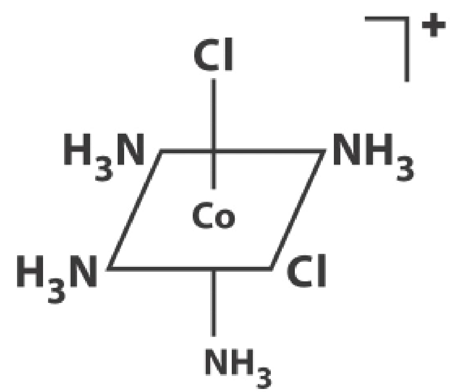
Cl^-



Cl^-



(a) *trans*-$[CoCl_2(NH_3)_4]^+$



(b) *cis*-$[CoCl_2(NH_3)_4]^+$