19 Transition metals and coordination chemistry

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※ Transition metals in general

✓ Importance

Cr	stainless steel
Mn	steelmaking
Pt, Pd	catalysts
Fe	transport of oxygen
	nitrogen fixation (Mo also)
Zn	catalyst in biological system
Co	vitamin B_{12}

✓ Similarity within a period

adding inner d, f electrons: less effect on chemistry

lanthanides and actinides

✓ Metallic

Ag best heat conductor of heat and e^-

Cu the second

✓ Ionic compounds

often contain more than one oxidation state

✓ Forms complex ions

usually colored: electron transition between *d* orbitals

often paramagnetic: contain unpaired electrons

✓ Electron configurations and oxidation states

The first row

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	$4s^2 3d^1$	$4s^2 3d^2$		$4s^1 3d^5$				$4s^2 3d^8$	$4s^1 3d^{10}$	$4s^2 3d^{10}$
Oxid state	3+							2+		2+

V–Mn: Contain higher oxid states

Fe–Zn: Higher nuclear charge: less higher oxid states

Ex. Mn: 2+, 3+, 4+, 7+

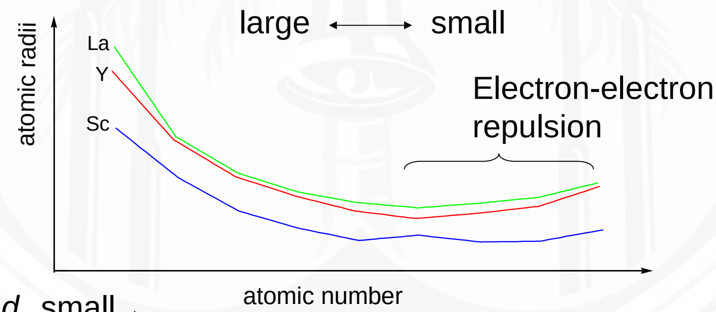
2+ is very common
due to loss of two 4*s* electrons

✓ Oxidation potential

large ⟷ small

stronger reducing ability

✓ Size



3*d* small

4*d* large

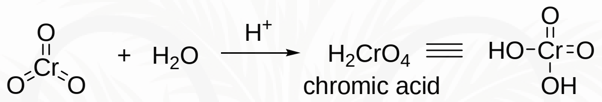
big change

5*d*

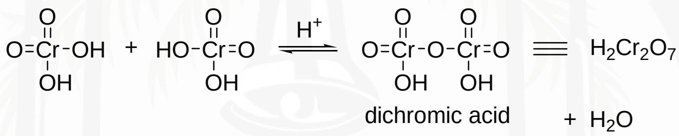
Similar: lanthanide contraction
Filling inner 4*f* orbitals
small effect on size
Increasing nuclear charge
offsets the increase of *n*

※ The first-row transition metals

- ✓ Sc Rare
- ✓ Ti Low density and high strength
  Titanium oxide (TiO_2) – white paint
  $TiCl_4$ – a strong Lewis acid
  $$TiCl_4(l) + 2H_2O(l) \rightarrow TiO_2(s) + 4HCl(g)$$
- ✓ V Used mostly in alloys
  V_2O_5 used as catalyst
- ✓ Cr Used in steel making
  As oxidizing agent: CrO_3 (chromium trioxide)



chromate ion: yellow colored



dichromate ion: orange → Cr^{3+}: green

- ✓ Mn Used in steel making
  $KMnO_4$: potassium permangnate (purple color)
  – strong oxidizing agent
  ↓
  MnO_2 (brown ppt)
- ✓ Fe Oxidized easily – rust: Fe_2O_3

  Fenton reaction:
  $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH$
  $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + \cdot OOH$

✓ Co Relatively rare; used in steel making
$CoSO_4$: dark blue

✓ Ni Abundant; good conductor
Resist to corrosion – used in plating

✓ Cu Good conductor; resistant to corrosion

$3Cu(s) + 2H_2O(l) + SO_2(g) + 2O_2(g) \rightarrow Cu_3(OH)_4SO_4(s)$

basic copper sulfate
銅綠

$Cu(H_2O)_6^{2+}$: blue color

✓ Zn Used as reducing agent and plating

※ Coordination compounds

L
L: Metal^{n+}:L Y^{n-} ← Counter ion
L

$M^{n+} + mL \leftrightarrows (ML_m)^{n+}$ $K_{complex}$

Ligand
using lone electron pair to form a bond to a metal ion

Donor atom
atom of the ligand bound to the metal ion

Coordination number
the number of donor atoms
Ex. $[Co(NH_3)_5Cl]Cl_2$: Co^{3+} has a coordination # of 6

For the same metal

coordination number varies

depends on size and nature of the ligand

4 and 6 are the most common

$[FeF_6]^{3-}$ $[FeCl_4]^{-}$

Larger size

$[Ni(NH_3)_6]^{2+}$ $[Ni(CN)_4]^{2-}$

neutral with negative charge

✓ Geometry

coordination 4: tetrahedral or square planar

More common

d^8: Pt(II), Au(III)

d^9: Cu(II)

coordination 6: octahedral

◎ Ligands

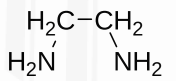
Monodentate ligand (單牙配基): forms one bond

Bidentate ligand: forms two bonds

Polydentate ligand

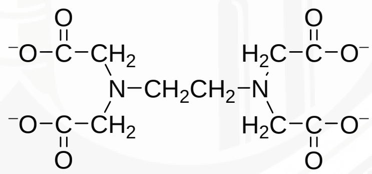
} chelates (螯合物)

Ex.



ethylenediamine

(en)



ethylenediaminetetraacetate

(EDTA)

Produce 6 coordination

Chelating agents form more stable complexes

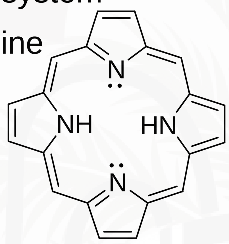
$$[Ni(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \leftrightarrows [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$
$$K_f = 4 \times 10^8$$

$$[Ni(H_2O)_6]^{2+}(aq) + 3en(aq) \leftrightarrows [Ni(en)_3]^{2+}(aq) + 6H_2O(l)$$
$$K_f = 2 \times 10^{18}$$

✓ Use: sequester metal ions
complex metal ions in hard water
remove Hg^{2+}, Pb^{2+}, Cd^{2+}

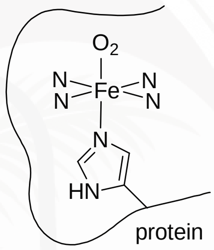
✓ Living system

Porphine



Heme: Fe^{2+}

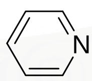
Chlorophyll: Mg^{2+}



◎ Nomenclature

Ex. $[Co(NH_3)_5Cl]Cl_2$
pentaamminechlorocobalt(III) chloride

Rules
- Cation before anion
- Ligands before metal (in formula: metal first)
  arrange in alphabetical order
  (prefix does not count)
- Anionic ligands end in O

Anionic		Neutral	
N_3^-	azido	NH_3	ammine
Br^-	bromo	H_2O	aqua
OH^-	hydroxo	CO	carbonyl
CO_3^{2-}	carbonato	NO	nitrosyl
$C_2O_4^{2-}$	oxalato		
CN^-	cyano		pyridine

- Oxidation number in ( )
- Prefix

mono	1
di	2
tri	3
tetra	4
penta	5
hexa	6

- With complicated ligand name

bis( )	2
tris( )	3
tetrakis( )	4
:	

Ex. $[Co(en)_3]Cl_3$ tris(ethylenediamine)cobalt(III) chloride

- Complex is anion: end in -ate

Ex. $K_4[Fe(CN)_6]$ potassium hexacyanoferrate(II)

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※ Isomerism

Structural isomerism: different bonding
Stereoisomerism: different space arrangement

◎ Structural isomerism

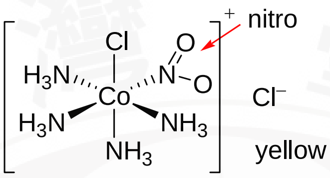
✓ Coordination isomerism

$[Cr(NH_3)_5SO_4]Br$ and $[Cr(NH_3)_5Br]SO_4$

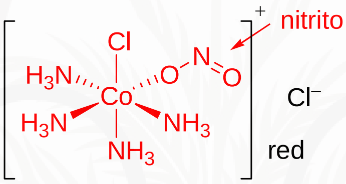
Ex. $CrCl_3(H_2O)_6$

$[Cr(H_2O)_6]Cl_3$	$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$	$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$
violet	green	green

✓ Linkage isomerism



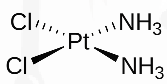
tetramminechloronitrocobalt(III) chloride



tetramminechloronitritocobalt(III) chloride

◎ Stereoisomerism

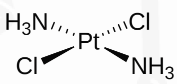
✓ Geometrical isomers



cis

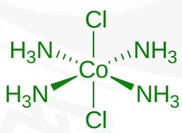
yellow

(cisplatin: a cancer drug)



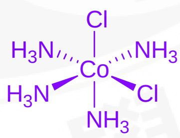
trans

pale yellow



trans

green



cis

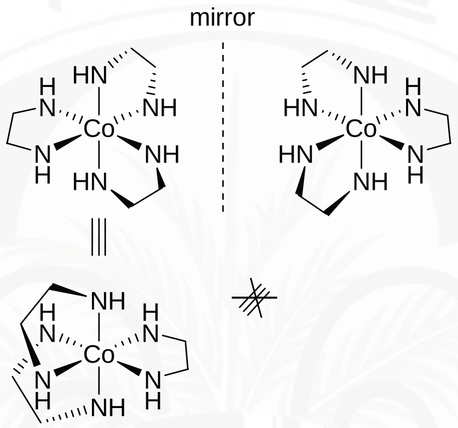
violet

✓ Optical isomers

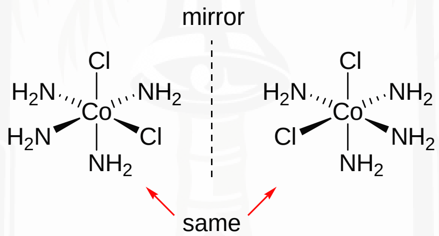
Enantiomers (對掌體;鏡像異構)

Mirror images but not superimposable

(Compounds with this property are chiral (掌性的))



achiral



(contain a plane of symmetry: must be achiral)

Properties of enantiomers

Most physical and chemical properties are the same

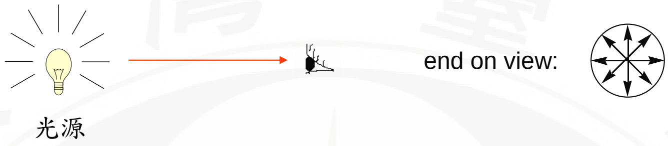
Rotate plane polarized light in different direction

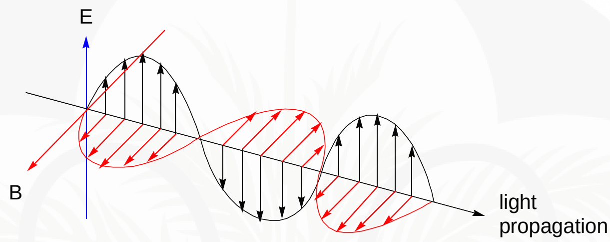
平面偏極光

◎ Plane-polarized light?

Ordinary light

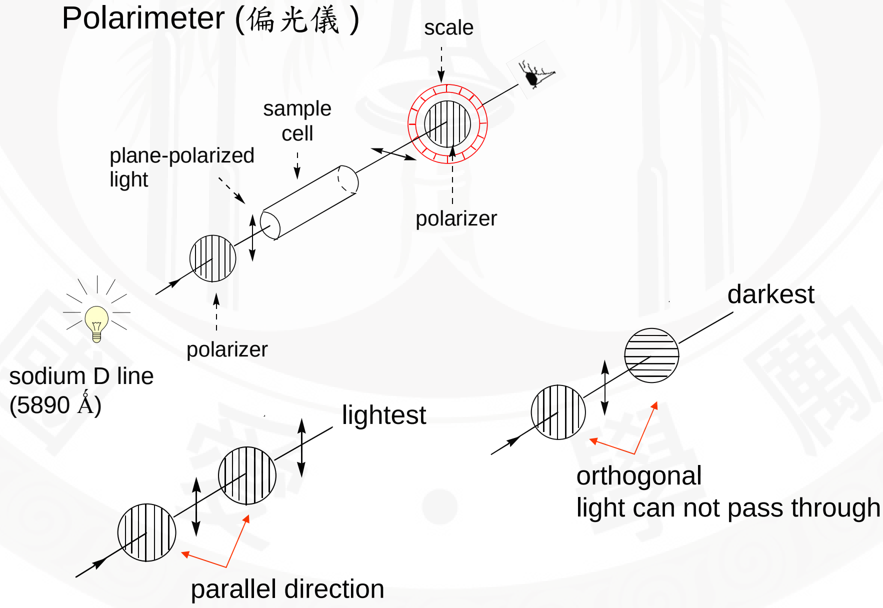
— composed of an infinite # of plane polarized light



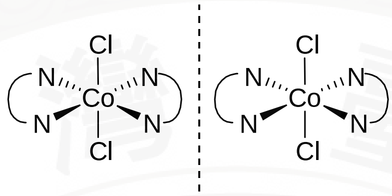


Plane-polarized light

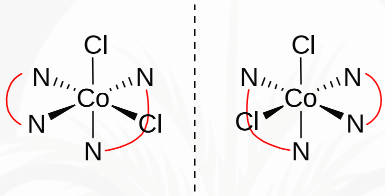
Polarimeter (偏光儀)



Ex.



same molecule



enantiomeric

※ Magnetic properties

✓ One electron

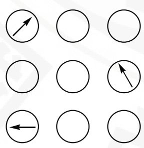
Possesses magnetic moment

✓ Two paired electron

Magnetic moment cancelled

⇨ diamagnetic ← Repelled in a magnetic field

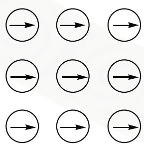
✓ With isolated unpaired electrons – paramagnetic



in a magnetic field: align with the field

→ net attractive

✓ With interactive unpaired electrons – ferromagnetic



The most stable form: align in the same direction

Interact strongly with magnetic field

Can form permanent magnet (Fe, Co, Ni)

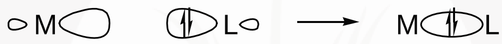
※ Bonding in complex ion

◎ The localized electron model
based on the valence bond theory

M–L

Considered as covalent bond

Can be viewed as



Lewis acid   Lewis base

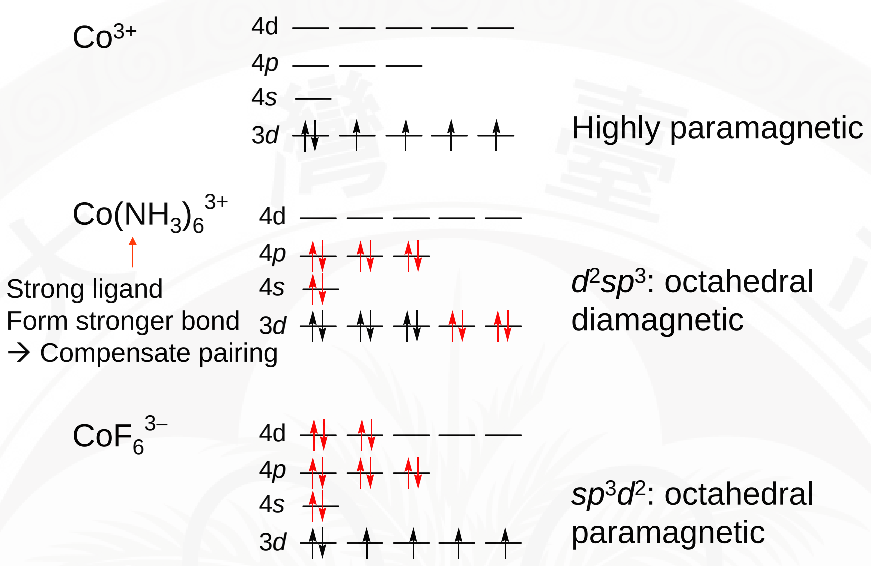
Number of hybridized metal orbitals = Number of ligands

Ex. $Co(NH_3)_6^{3+}$ coordination # = 6
→ d^2sp^3
→ octahedral

$CoCl_4^{2-}$ coordination # = 4
→ sp^3
→ tetrahedral

$Ni(CN)_4^{2-}$ coordination # = 4
→ dsp^2
→ square planar

$Ag(NH_3)_2^{+}$ coordination # = 2
→ sp
→ linear



◎ The crystal field model

A theory developed for the energy relationships of ions in cystals – focuses on the energies of *d* orbitals

Color and magnetic properties of transition metals:

related to *d* orbitals

Interaction between ions and ligands:

Electronic attraction and repulsion

Only ionic bonding is considered

Interaction of *L* e^-s and the *M* ion is NOT considered

Five *d* orbitals

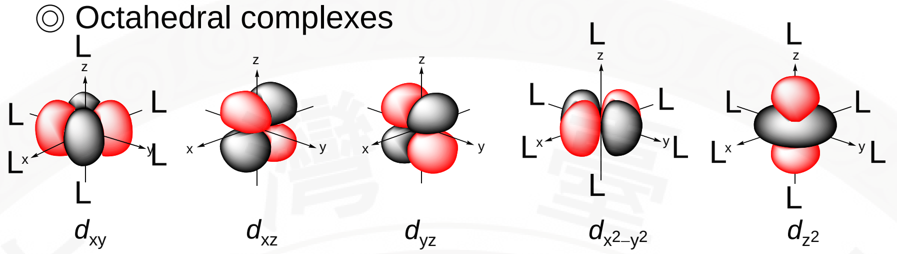
same E when not used in bonding

When ligands approach

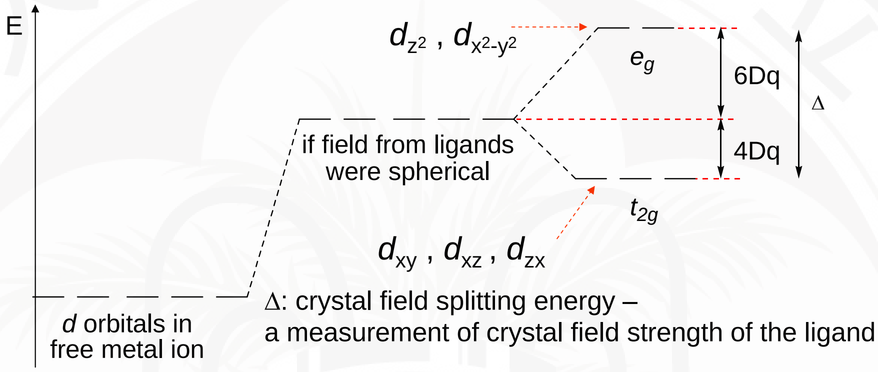
repulsions occur between

ligand electrons and *d* orbital electrons

◎ Octahedral complexes



The repulsive interactions in d_{z^2} and $d_{x^2-y^2}$ are the highest



Δ: crystal field splitting energy –
a measurement of crystal field strength of the ligand

Ex. Co^{3+} Strong field (large Δ) Weak field (small Δ)

Low spin High spin

Spectrochemical series

$CN^- > NO_2^- > en > NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-$

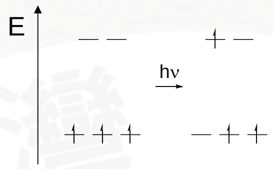
Strong field ligands Weak field ligands

Strong field ligand → low spin complex

Weak field ligand → high spin complex

⇨ $Co(NH_3)_6^{3+}$: diamagnetic CoF_6^{3-}: paramagnetic

Ex. Cr^{3+}



$[Cr(H_2O)_6]Cl_3$ violet

weaker L → smaller Δ → absorbs longer wavelength

$[Cr(NH_3)_6]Cl_3$ yellow

stronger L → larger Δ → absorbs shorter wavelength

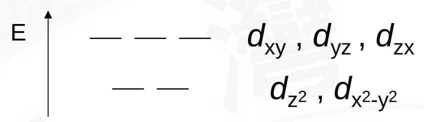
absorbed λ (nm)	absorbed color	transmitted color
400	violet	greenish yellow
450	blue	yellow
570	yellow-green	violet
650	red	green

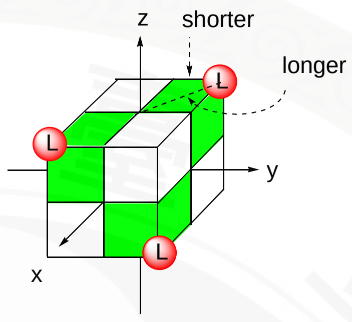
Note: For a given ligand
As charge on the metal ion increases
→ weak-field ligand may become strong field
(M-L distance smaller)

Ex. NH_3 is a weak ligand for Co^{2+}
but a strong field ligand for Co^{3+}

Drawn closer
→ Larger repulsion

◎ Tetrahedral crystal field



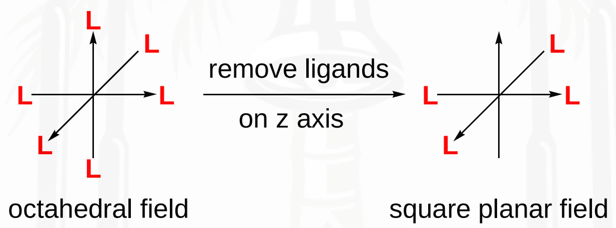


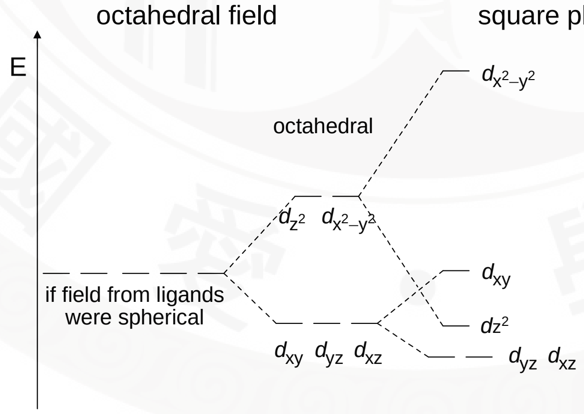
None of the 3*d* orbitals
points to the ligands

Δ is smaller than octahedral field
→ Always high spin

Tetrahedral complexes are more likely
for nontransition metals
and transition metals with no crystal field stabilization
(d^0, high spin d^5, and d^{10})
Ex. $TiCl_4$, $FeCl_4^-$, $ZnCl_4^{2-}$

◎ Square planar field

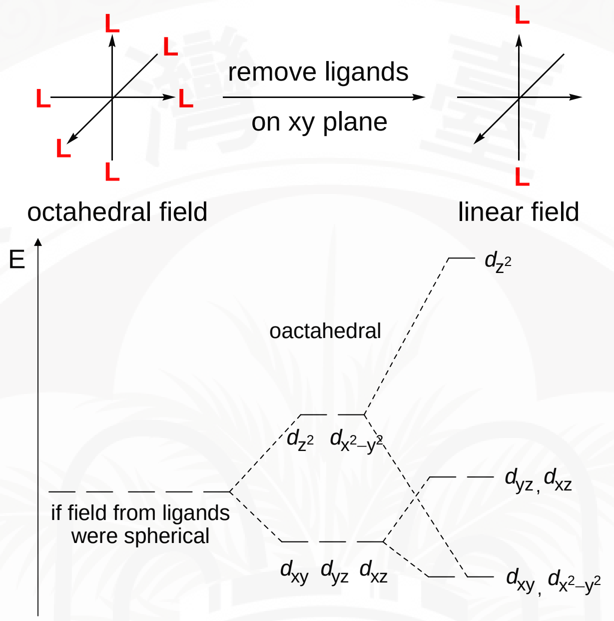




Favor stronger L
Characteristic
for d^8, d^7, and d^9

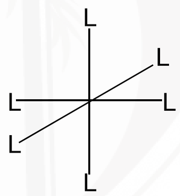
$[NiCl_4]^{2-}$: tetrahedral
$[Ni(CN)_4]^{2-}$: square planar

◎ Linear field

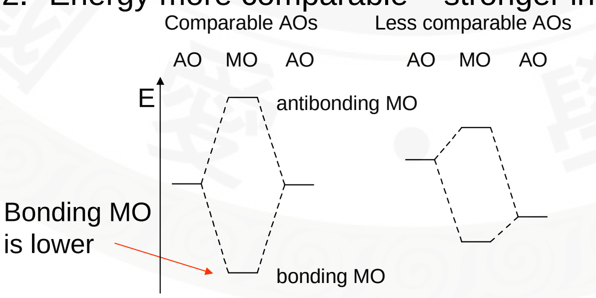


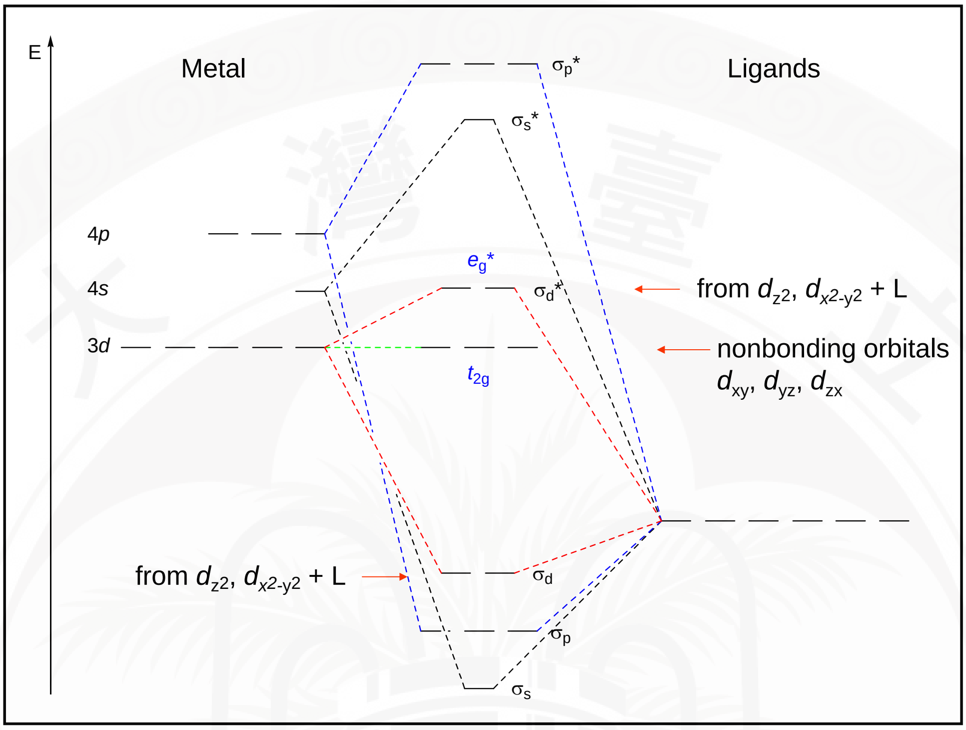
※ The MO model

Considering octahedral complex, ML_6^{n+}



1. s overlaps with all Ls
   p_x, p_y, p_z each overlaps with two Ls
   d_{z^2} overlaps with all Ls
   $d_{x^2-y^2}$ overlaps with four Ls
   d_{xy}, d_{yz}, d_{zx} have no overlaps with Ls
2. Energy more comparable – stronger interaction





With strong electron withdrawing ligands
⇨ Ligand orbitals have lower E
⇨ Less comparable with metal ion orbitals
⇨ e_g* is lower (t_{2g} stays at the same level)
⇨ Δ is smaller
⇨ Higher spin

Ex. CoF_6^{3-}
fluorine has lower energy level
⇨ small Δ
⇨ high spin

$Co(NH_3)_6^{3-}$
NH_3 has higher lone pair orbitals
⇨ better interaction
⇨ higher e_g*, larger Δ
⇨ low spin

※ Biological importance

Transition metals easily undergo oxid. and red.

- electron transfer
- transport and storage of O_2
- as catalysts and drugs

Iron in cytochrome c
(細胞色素)