Chapter 21:

Transition Metals and Coordination Chemistry

鐵 —— 鋼鐵
銅 —— 電線、水管
鈦 —— 塗料
銀 —— 照相底片
Mg, Cr, V, Co —— 鋼鐵添加物
Pt —— 工業及汽車用催化劑

TABLE 21.1 Some Transition Metals Important to the U.S. Economy and Defense

Metal	Uses	Percentage Imported
Chromium	Stainless steel (especially for parts exposed to corrosive gases and high temperatures)	~91%
Cobalt	High-temperature alloys in jet engines, magnets, catalysts, drill bits	~93%
Manganese	Steelmaking	~97%
Platinum and palladium	Catalysts	~87%

過渡金屬離子在生物體組織上的重要性：

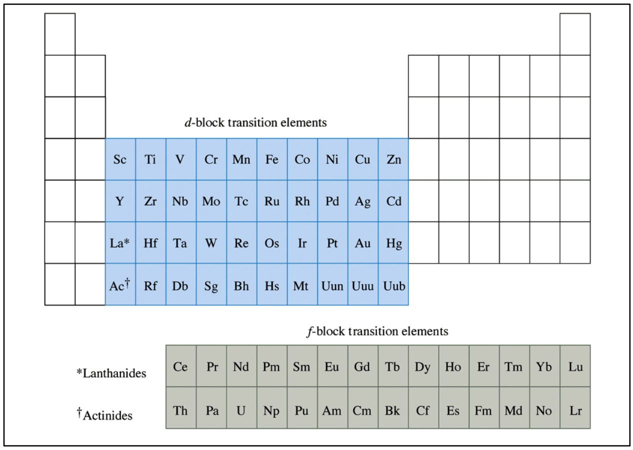
Fe complexes：**提供**O_2**的運輸及儲存**
Mo and Fe complexes: nitrogen fixation**的催化劑**
Zn: **存在於人體**150**種以上的生物分子**
Cu, Fe: **在呼吸循環上扮演重要角色**
Co:**存在於基本的生物分子，例如維他命**B12

21.1 Transition Metals

show great similarities within a given period as well as within a given vertical group.

Key reason: last electrons added are inner electrons (*d*'s, *f*'s).

Figure 21.1: The position of the transition elements on the periodic table.



過渡金屬性質的多樣化：

1. 展現典型的金屬性質，具有金屬光澤，及相對上高的導電、及導熱性。例如Cu, Ag

2. W melting point: 3400 °C; Hg: liquid at 25 °C

   Fe, Ti: hard; Cu, Au, Ag: soft

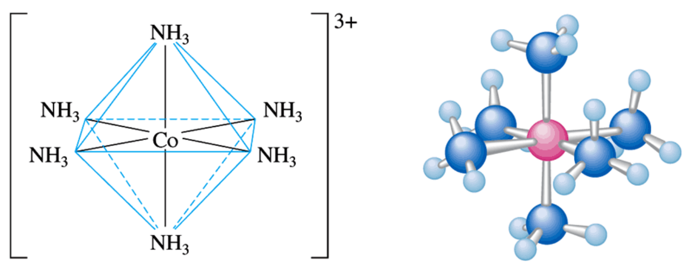
   Cr, Ni, Co…等的氧化物會附著在金屬表面;
   Fe的氧化物會剝落;
   Au, Ag, Pt, Pd 不會形成氧化物

3. 含有一種以上的氧化態

Complex Ions

species where the transition metal ion is surrounded by a certain number of ligands (Lewis bases).

$Co(NH_3)_6^{3+}$ $Pt(NH_3)_3Br^+$



The $Co(NH_3)_6^{3+}$ ion

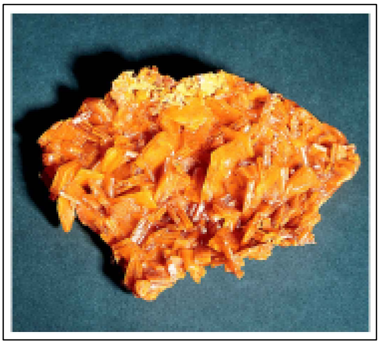
A Coordination Compound

typically consists of a complex ion and counter ions (anions or cations as needed to produce a neutral compound).

$[Co(NH_3)_5Cl]Cl_2$

$[Fe(en)_2(NO_2)_2]_2SO_4$

過渡金屬錯化合物大部分具有顏色



$PbMoO_4$　　$MnCO_3$

過渡金屬錯化合物大部分具有顏色

(From left to right) Metals containing the metal ions Co^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}, and Ni^{2+}.

TABLE 21.2 Selected Properties of the First-Row Transition Metals

	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
Atomic number	21	22	23	24	25	26	27	28	29	30
Electron configuration*	$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$	$4s^23d^{10}$
Atomic radius (pm)	162	147	134	130	135	126	125	124	128	138
Ionization energies (eV/atom)										
First	6.54	6.82	6.74	6.77	7.44	7.87	7.86	7.64	7.73	9.39
Second	12.80	13.58	14.65	16.50	15.64	16.18	17.06	18.17	20.29	17.96
Third	24.76	27.49	29.31	30.96	33.67	30.65	33.50	35.17	36.83	39.72
Reduction potential† (V)	−2.08	−1.63	−1.2	−0.91	−1.18	−0.44	−0.28	−0.23	+0.34	−0.76
Common oxidation states	+3	+2, +3, +4	+2, +3, +4, +5	+2, +3, +6	+2, +3, +4, +7	+2, +3	+2, +3	+2	+1, +2	+2
Melting point (°C)	1397	1672	1710	1900	1244	1530	1495	1455	1083	419
Density (g/cm^3)	2.99	4.49	5.96	7.20	7.43	7.86	8.9	8.90	8.92	7.14
Electrical conductivity‡	—	2	3	10	2	17	24	24	97	27

Figure 21.2: Plots of the first (red dots) and third (blue dots) ionization energies for the first-row transition metals.

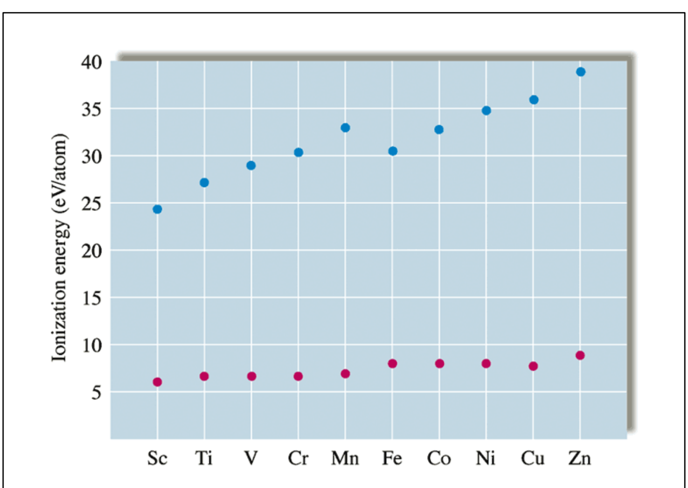


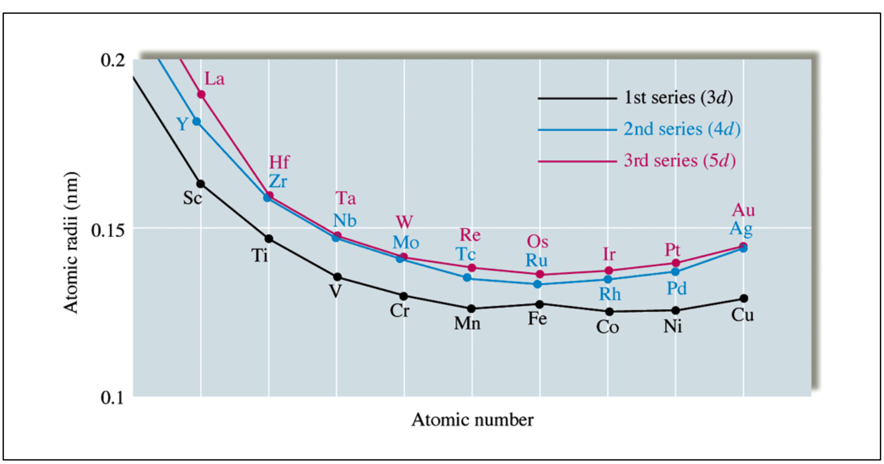
TABLE 21.3
Relative Reducing Abilities of the First-Row Transition Metals in Aqueous Solution

Reaction	Potential (V)
$Sc \rightarrow Sc^{3+} + 3e^-$	2.08
$Ti \rightarrow Ti^{2+} + 2e^-$	1.63
$V \rightarrow V^{2+} + 2e^-$	1.2
$Mn \rightarrow Mn^{2+} + 2e^-$	1.18
$Cr \rightarrow Cr^{2+} + 2e^-$	0.91
$Zn \rightarrow Zn^{2+} + 2e^-$	0.76
$Fe \rightarrow Fe^{2+} + 2e^-$	0.44
$Co \rightarrow Co^{2+} + 2e^-$	0.28
$Ni \rightarrow Ni^{2+} + 2e^-$	0.23
$Cu \rightarrow Cu^{2+} + 2e^-$	−0.34

Reducing ability ↑

除了銅以外，所有的金屬都可以將1M的H^+離子還原成H_2氣體

Figure 21.3: Atomic radii of the *3d*, *4d*, and 5d transition series.



半徑的一般傾向

1. 隨週期表由左至右逐漸減少
2. 由於鑭系縮收的結果4d及5d元素的半徑大小類似

由於半徑大小類似， 4d及5d元素有非常相似的化學性質。元素的差異性隨著週期表往右而漸增，例如Nb與Ta非常類似，但是不如Zr與Hf類似。

4d及5d元素的應用：

1. Zr, ZrO_2與Nb, Mo的合金: 抗高溫，用於太空梭零件。
2. Nb, Mo :鋼材中重要的合金物質。
3. Ta: 抗體液，用於人工骨骼。
4. Ru, Os, Rh, Ir, Pd, Pt: 工業製程上的催化劑。

21.2 The First-Raw Transition Metals

Sc

1. 稀有元素
2. 通常以+3價氧化態存在於化合物中
3. 大部分化合物無色(+3價沒有d電子)，逆磁性
4. 曾被用於電子裝置，例如高密度燈泡

Ti

1. 廣泛分佈於地殼中 (0.6% by mass)
2. 相對上低密度、高強度、耐高溫 —— 用於噴射機引擎
3. 抗拒化學物質攻擊—— 用於管線、馬達、化學反應槽
4. 常以+4價氧化態存在，例如TiO2 (白色固體), TiCl4 (無色液體)
5. Ti^{3+}在水溶液中以$Ti(H_2O)_6^{3+}$存在，呈紫色

TiO_2

1. 白色色素，用於紙張、塗料、地毯 、塑膠 、合成纖維 、白色輪胎 、化妝品(遮光劑)

V

1. 廣泛分佈於地殼中 (0.02% by mass)
2. V_2O_5用於生產硫酸的催化劑
3. V金屬具灰藍色，硬度高，耐腐蝕
4. 合金鋼鐵用於引擎零件及輪軸製造
5. 主要氧化態+5價，而+5　+2價氧化態都存在於水溶液中

TABLE 21.4
Oxidation States and Species for Vanadium in Aqueous Solution

Oxidation State of Vanadium	Species in Aqueous Solution
+5	VO_2^+ (yellow)
+4	VO^{2+} (blue)
+3	$V^{3+}(aq)$ (blue-green)
+2	$V^{2+}(aq)$ (violet)

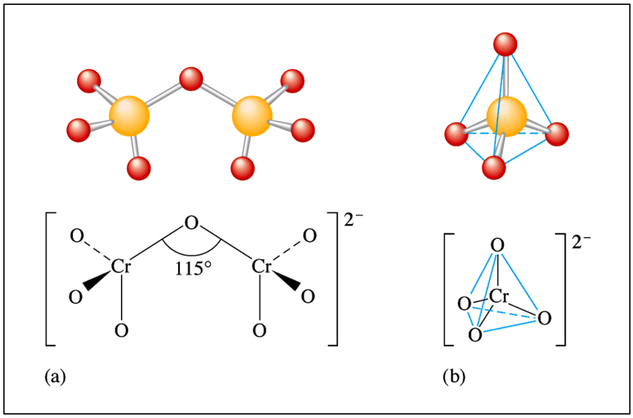
Cr

1. 相對上較稀少
2. 通常形成+2、+3、+4、及+6價化合物，Cr^{2+}是很強的還原劑，可以將水中O_2的移除。Cr^{6+}是很好的氧化劑，在酸性溶液中會被還原成Cr^{3+}。

TABLE 21.5
Typical Chromium Compounds

Oxidation State of Chromium	Examples of Compounds (X = halogen)
+2	CrX_2
+3	CrX_3 Cr_2O_3 (green) $Cr(OH)_3$ (blue-green)
+6	$K_2Cr_2O_7$ (orange) Na_2CrO_4 (yellow) CrO_3 (red)

Figure 21.4: The structures of the chromium(VI) anions: (a) $Cr_2O_7^{2-}$, which exists in acidic solution, and (b) CrO_4^{2-}, which exists in basic solution.



Mn

1. 含量上相對豐富(0.1% of the earth's crust)
2. 用於製造岩石壓碎機、銀行金庫、裝甲鋼板等特別硬的鋼材
3. +7 +2價氧化態都存在，其中於+7及 +2價最常見。 Mn^{2+} 與所有常見陰離子形成鹽類。在水溶液中Mn^{2+}形成淡粉紅色$Mn(H_2O)_6^{2+}$。

TABLE 21.6
Some Compounds of Manganese in Its Most Common Oxidation States

Oxidation State of Manganese	Examples of Compounds
+2	$Mn(OH)_2$ (pink)
	MnS (salmon)
	$MnSO_4$ (reddish)
	$MnCl_2$ (pink)
+4	MnO_2 (dark brown)
+7	$KMnO_4$ (purple)

Fe

1. 含量最豐富的重金屬
   (4.7% of the earth's crust)
2. 白色、光亮、硬度不大
3. 在潮濕的空氣中快速的被氧氧化，形成鐵銹
4. 在化合物中以+2及 +3價氧化態存在
5. 水合物$Fe(H_2O)_6^{2+}$呈現淡綠色，　$Fe(H_2O)_6^{3+}$無色

TABLE 21.7
Typical Compounds of Iron

Oxidation State of Iron	Examples of Compounds
+2	FeO (black) FeS (brownish black) $FeSO_4 \cdot 7H_2O$ (green) $K_4Fe(CN)_6$ (yellow)
+3	$FeCl_3$ (brownish black) Fe_2O_3 (reddish brown) $K_3Fe(CN)_6$ (red) $Fe(SCN)_3$ (red)
+2, +3 (mixture)	Fe_3O_4 (black) $KFe[Fe(CN)_6]$ (deep blue, "Prussian blue")

Co

1. 用於製造不銹鋼及鎢鉻鈷合金
2. 在化合物中主要以+2及 +3價氧化態存在

TABLE 21.8
Typical Compounds of Cobalt

Oxidation State	Examples of Compounds
+2	$CoSO_4$ (dark blue) $[Co(H_2O)_6]Cl_2$ (pink) $[Co(H_2O)_6](NO_3)_2$ (red) CoS (black) CoO (greenish brown)
+3	CoF_3 (brown) Co_2O_3 (charcoal) $K_3[Co(CN)_6]$ (yellow) $[Co(NH_3)_6]Cl_3$ (yellow)

Ni

1. 在地殼中含量排列第24
2. 銀白色，具有高導電性、及高導熱性。非常抗腐蝕，用於放置活性較高的金屬，也被使用在合金的製造
3. 在化合物中幾乎以+2價氧化態存在

TABLE 21.9 Typical Compounds of Nickel

Oxidation State of Nickel	Examples of Compounds
+2	$NiCl_2$ (yellow) $[Ni(H_2O)_6]Cl_2$ (green) NiO (greenish black) NiS (black) $[Ni(H_2O)_6]SO_4$ (green) $[Ni(NH_3)_6](NO_3)_2$ (blue)

Cu

1. 廣泛的分佈在含S, As, Cl,及碳酸鹽的礦物中
2. 具有高導電性及抗腐蝕性，用於鉛管及電子上的應用方面，及合金的製造
3. 在空氣中慢慢腐蝕，形成銅綠
4. 在化合物中以+1及 +2價氧化態存在，而主要為+2價
5. 微量的Cu為生命所必需，大量的Cu則有劇毒

TABLE 21.10 Alloys Containing Copper

Alloy	Composition (% by mass in parentheses)
Brass	Cu (20–97), Zn (2–80), Sn (0–14), Pb (0–12), Mn (0–25)
Bronze	Cu (50–98), Sn (0–35), Zn (0–29), Pb (0–50), P (0–3)
Sterling silver	Cu (7.5), Ag (92.5)
Gold (18-karat)	Cu (5–15), Au (75), Ag (10–20)
Gold (14-karat)	Cu (12–28), Au (58), Ag (4–30)

TABLE 21.11
Typical Compounds of Copper

Oxidation State of Copper	Examples of Compounds
+1	Cu_2O (red)
	Cu_2S (black)
	CuCl (white)
+2	CuO (black)
	$CuSO_4 \cdot 5H_2O$ (blue)
	$CuCl_2 \cdot 2H_2O$ (green)

Zn

1. 廣泛的分佈於地殼中
2. 白色、光澤、活性強，是很好的還原劑
3. 約90%使用於鍍鋅鋼鐵

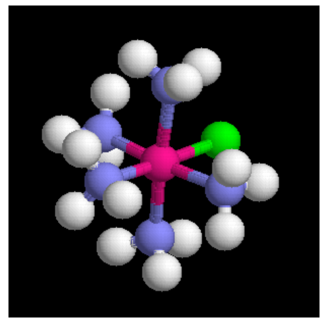
21.3 Coordination Compounds

typically consists of a complex ion and counter ions (anions or cations as needed to produce a neutral compound).

$[Co(NH_3)_5Cl]Cl_2$

$[Fe(en)_2(NO_2)_2]_2SO_4$

$Na_3[Mo(CO)_3(CN)_3]$

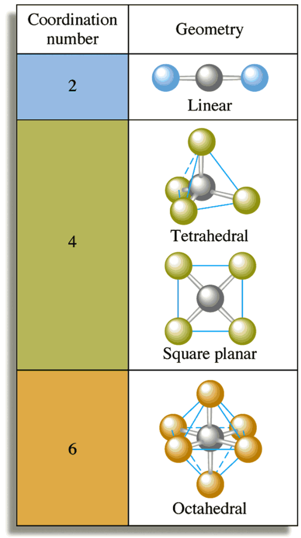


Coordination Number

TABLE 21.12 Typical Coordination Numbers for Some Common Metal Ions

M^+	Coordination Numbers	M^{2+}	Coordination Numbers	M^{3+}	Coordination Numbers
Cu^+	2, 4	Mn^{2+}	4, 6	Sc^{3+}	6
Ag^+	2	Fe^{2+}	6	Cr^{3+}	6
Au^+	2, 4	Co^{2+}	4, 6	Co^{3+}	6
		Ni^{2+}	4, 6		
		Cu^{2+}	4, 6	Au^{3+}	4
		Zn^{2+}	4, 6		

Figure 21.5: The ligand arrangements for coordination numbers 2, 4, and 6.



A Ligand

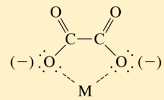
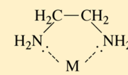
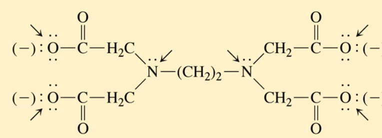
a neutral molecule or ion having a lone electron pair that can be used to form a bond to a metal ion (Lewis base).

coordinate covalent bond: metal-ligand bond

monodentate ligand: one bond to metal ion

polydentate ligand (chelate): can form more than two bonds to a metal ion

TABLE 21.13 Some Common Ligands

Type	Examples
Unidentate/monodentate	H_2O CN^- SCN^- (thiocyanate) X^- (halides) NH_3 NO_2^- (nitrite) OH^-
Bidentate	Oxalate  Ethylenediamine (en) 
Polydentate	Diethylenetriamine (dien) $H_2N-(CH_2)_2-NH-(CH_2)_2-NH_2$ Three coordinating atoms Ethylenediaminetetraacetate (EDTA)  Six coordinating atoms

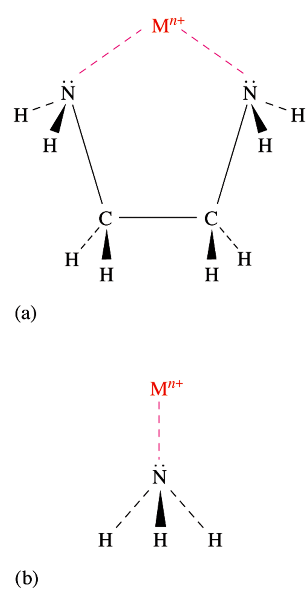
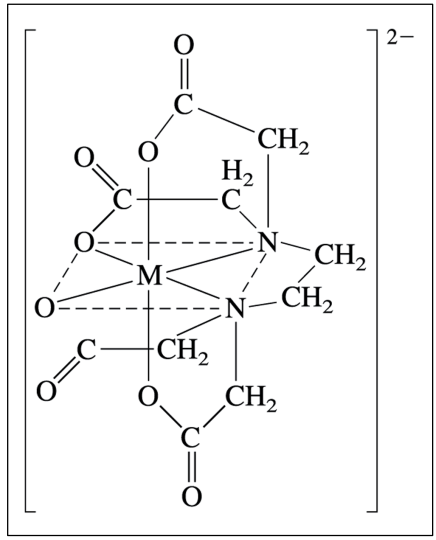


Figure 21.6:
(a) The bidentate ligand ethylenediamine can bond to the metal ion through the lone pair on each nitrogen atom, thus forming two coordinate covalent bonds.
(b) Ammonia is a monodentate ligand.

Figure 21.7:
The coordination of EDTA with a 2+ metal ion.



Naming Coordination Compounds

$[Co(NH3)_5Cl]Cl_2$

1. Cation is named before the anion.
   "chloride" goes last
2. Ligands are named before the metal ion.
   ammine, chlorine named before cobalt
3. For ligand, an "o" is added to the root name of an anion (fluoro, bromo). For neutral ligands the name of the molecule is used, with exceptions
   NH3, H2O, CO

TABLE 21.14
Names of Some Common Unidentate Ligands

Neutral Molecules	
Aqua	H_2O
Ammine	NH_3
Methylamine	CH_3NH_2
Carbonyl	CO
Nitrosyl	NO
Anions	
Fluoro	F^-
Chloro	Cl^-
Bromo	Br^-
Iodo	I^-
Hydroxo	OH^-
Cyano	CN^-

4. The prefixes mono-, di-, tri-, etc., are used to denote the number of simple ligands.

   pentaammine

5. The oxidation state of the central metal ion is designated by a (Roman numeral).

   cobalt (III)

6. When more than one type of ligand is present, they are named alphabetically.

   pentaamminechloro

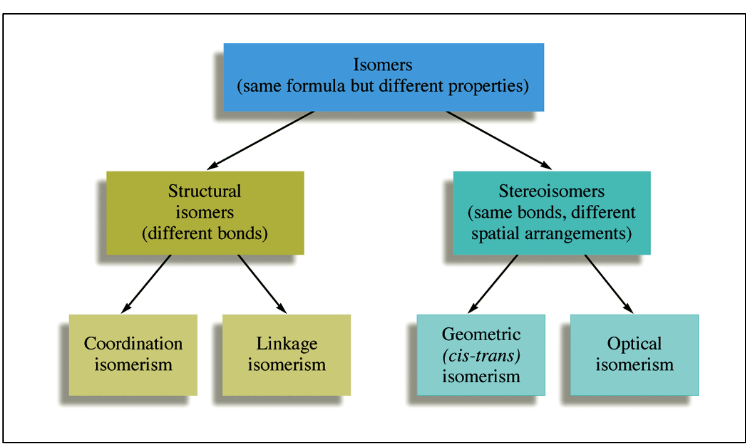
7. If the complex ion has a negative charge, the suffix “ate” is added to the name of the metal.

   pentaamminechlorocobalt (III) chloride

TABLE 21.15
Latin Names Used for Some Metal Ions in Anionic Complex Ions

Metal	Name in an Anionic Complex
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argentate
Gold	Aurate
Tin	Stannate

21.4 Isomerism



結構異構物：含有相同原子，但是有一個或多個不同的鍵結

立體異構物：所有鍵結都相同，但是原子的空間排列不同

Structure Isomerism

coordination isomerism: The composition of the complex ion varies.

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

$[Co(en)_3][Cr(ox)_3]$ and $[Cr(en)_3][Co(ox)_3]$

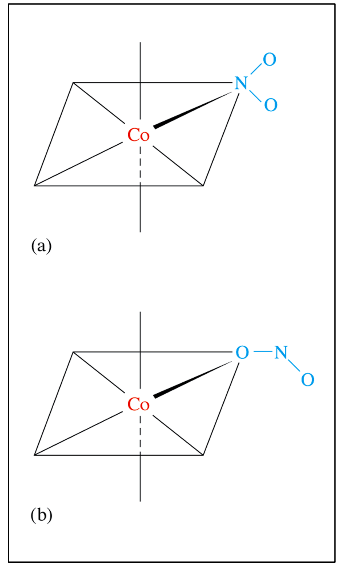
linkage isomerism: Same complex ion structure but point of attachment of at least one of the ligands differs.

$[Co(NH_3)_4(NO_2)Cl]Cl$ and $[Co(NH_3)_4(ONO)Cl]Cl$

yellow red

linkage isomerism

Figure 21.9: As a ligand, NO_2^- can bond to a metal ion (a) through a lone pair on the nitrogen atom or (b) through a lone pair on one of the oxygen atoms.



Stereoisomerism

geometrical isomerism (cis-trans): Atoms or groups of atoms can assume different positions around a rigid ring.

$Pt(NH_3)_2Cl_2$

optical isomerism: the isomers have opposite effects on plane-polarized light.

Figure 21.10: (a) The *cis* isomer of $Pt(NH_3)_2Cl_2$ (yellow). (b) The *trans* isomer of $Pt(NH_3)_2Cl_2$ (pale yellow).

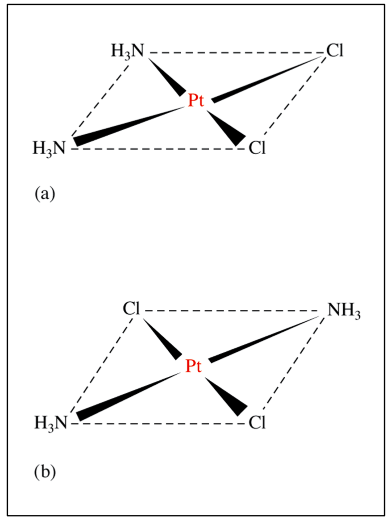


Figure 21.11: (a) The *trans* isomer of $[Co(NH_3)_4Cl_2]^+$. (b) The *cis* isomer of $[Co(NH_3)_4Cl_2]^+$.

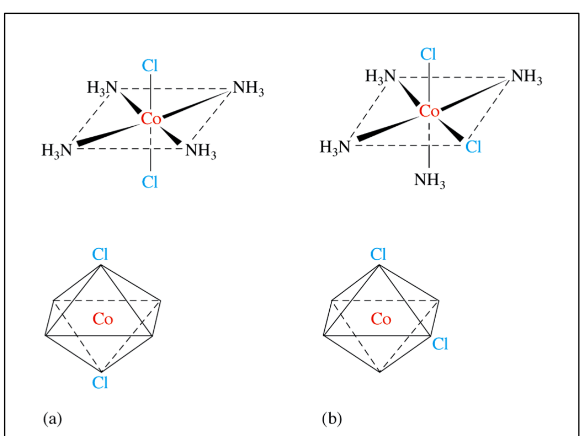


Figure 21.14: Some *cis* complexes of platinum and palladium that show significant antitumor activity.

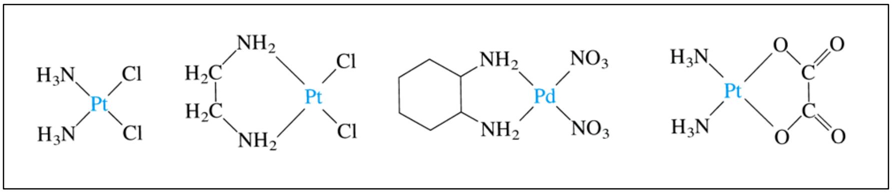


Figure 21.12: Unpolarized light consists of waves vibrating in many different planes (indicated by the arrows). The polarizing filter blocks all waves except those vibrating in a given plane.

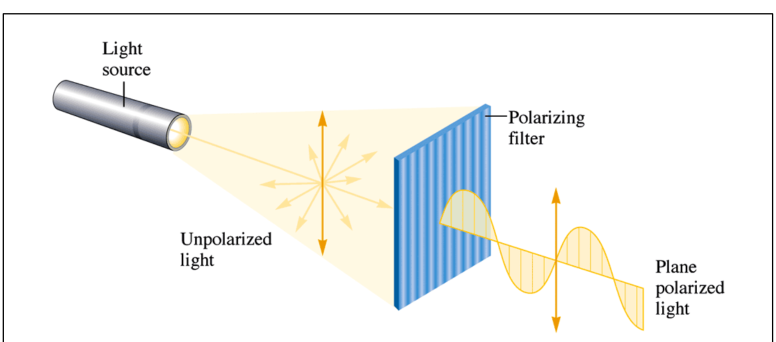


Figure 21.13: The rotation of the plane of polarized light by an optically active substance. The angle of rotation is called theta (θ).

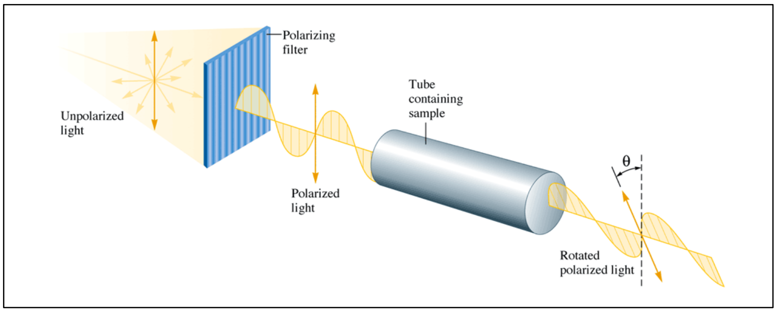


Figure 21.15: A human hand exhibits a nonsuperimposable mirror image. Note that the mirror image of the right hand (while identical to the left hand) cannot be turned in any way to make it identical to (superimposable on) the actual right hand.

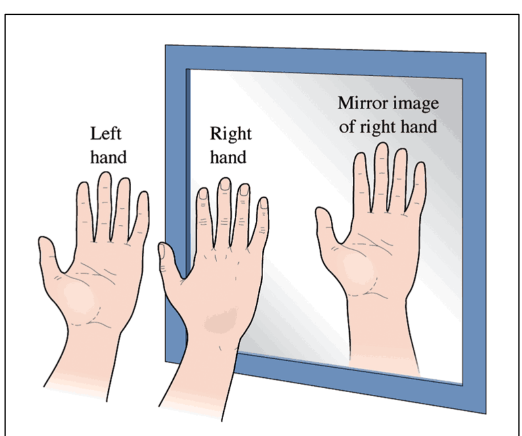
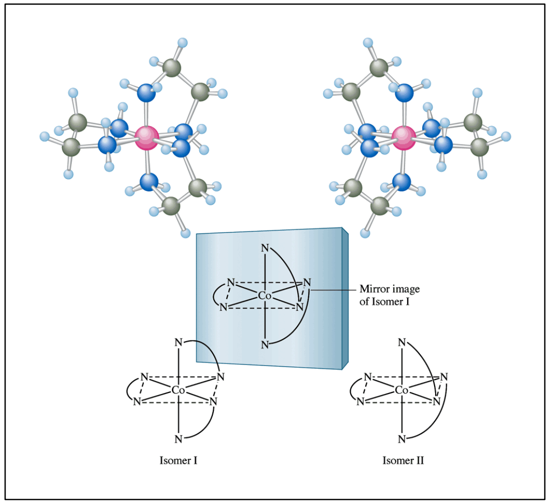


Figure 21.16: Isomers I and II of $Co(en)_3^{3+}$ are mirror images (the image of I is identical to II) that cannot be superimposed. That is, there is no way that I can be turned in space so that it is the same as II.



物體如果具有不可重疊的鏡像，則物體具有對掌性，
物體與它的鏡像互為鏡像異構物

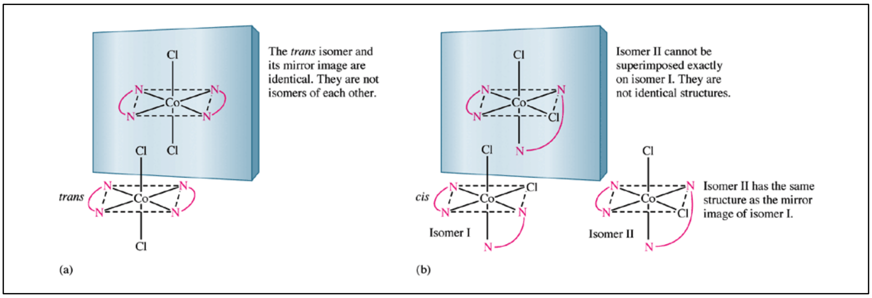
具有不可重疊鏡像的異構物稱為：enantiomers
會使平面極化光偏折，因此是光學異構物

使平面極化光轉向右邊的異構物稱為：dextrorotatory

使平面極化光轉向左邊的異構物稱為：levorotatory

含有等量 l 及 d form 異構物的混合(溶液)稱為：
racemic mixture，會彼此抵銷效應，不會使平面極化光偏折

Figure 21.17: (a) The *trans* isomer of $Co(en)_2Cl_2^+$ and its mirror image are identical (superimposable). (b) The *cis* isomer of $Co(en)_2Cl_2^+$ and its mirror image are not superimposable and are thus a pair of optical isomers



幾何異構物不一定是光學異構物

21.5 Bonding in Complex Ions: The Localized Electron Model

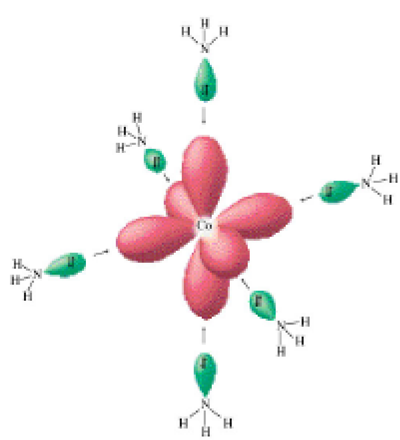


Figure 21.18: A set of six d^2sp^3 hybrid orbitals on Co^{3+} can accept an electron pair from each of six NH_3 ligands to form the $Co(NH_3)_6^{3+}$ ion.

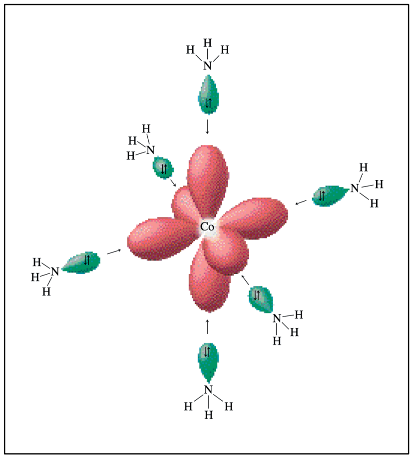
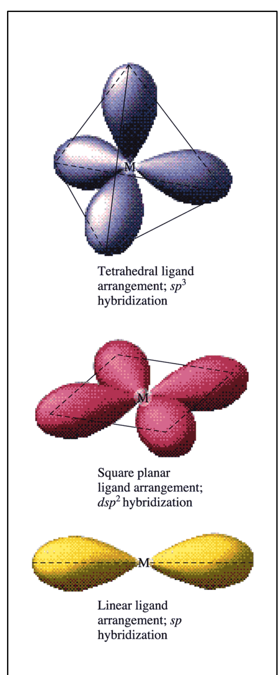


Figure 21.19:
The hybrid orbitals required for tetrahedral, square planar, and linear complex ions.



Valence bond theory

---- 利用coordinate covalent bond解釋鍵結，由 Pauling 在1930s提出，可以解釋分子形狀及磁性。

例： $PtCl_4^{2-}$ square planar, diamagnetic

$5d^8$

Pt^{2+} $\underline{\downarrow\uparrow}$ $\underline{\downarrow\uparrow}$ $\underline{\downarrow\uparrow}$ $\underline{\downarrow}$ $\underline{\downarrow\ \ }$

21.6 Crystal Field Model

focuses on the energies of the *d* orbitals.

Assumptions

1. Ligands are negative point charges.
2. Metal-ligand bonding is entirely ionic.

strong-field (low-spin): large splitting of *d* orbitals

weak-field (high-spin): small splitting of *d* orbitals

Figure 21.20: An octahedral arrangement of point-charge ligands and the orientation of the 3*d* orbitals.

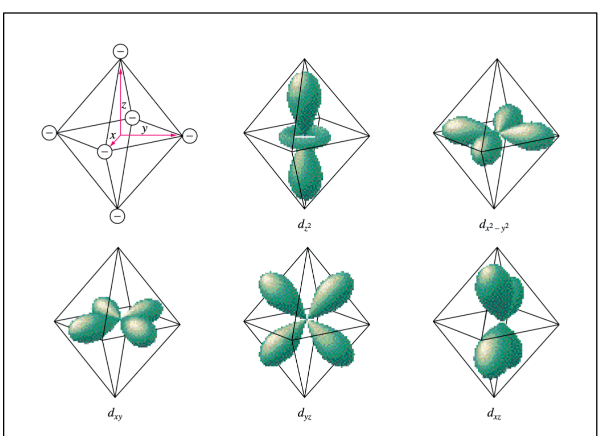


Figure 21.21: The energies of the 3*d* orbitals for a metal ion in an octahedral complex.

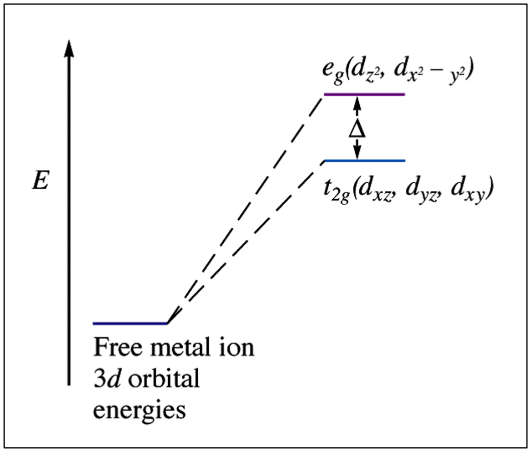
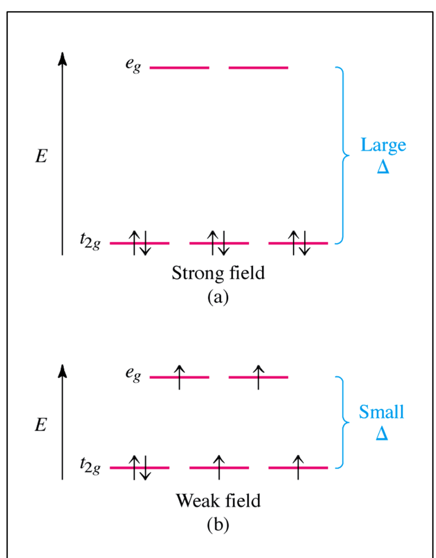


Figure 21.22: Possible electron arrangements in the split 3*d* orbitals in an octahedral complex of Co^{3+} (electron configuration $3d^6$). (a) In a strong field (large ? value), the electrons fill the t_{2g} set first, giving a diamagnetic complex. (b) In a weak field (small ? value), the electrons occupy all five orbitals before any pairing occurs.



例 (a) $Co(NH_3)_6^{3+}$； (b) CoF_6^{3-}

(a) Spectrochemical series:

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

Strong field weak field

(b) Δ 隨著metal ion的電荷增加而增加

$Co(NH_3)_6^{2+}$ weak-field complex

$Co(NH_3)_6^{3+}$ strong-field complex

(c) Δ值第二、三週期過渡金屬 >第一週期過渡金屬

Figure 21.23: The visible spectrum.

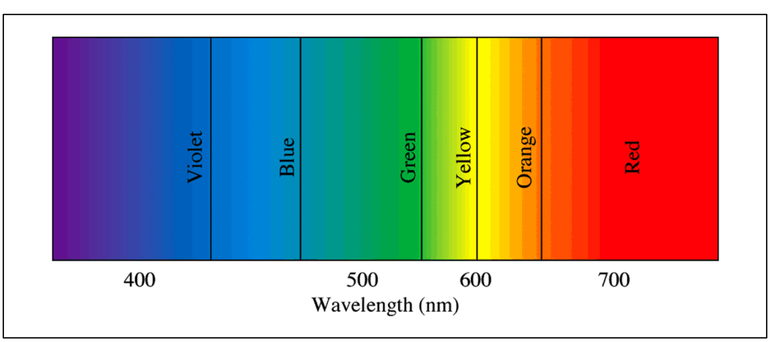


Figure 21.24:
(a) When white light shines on a filter that absorbs in the yellow-green region, the emerging light is violet. (b) Because the complex ion $Ti(H_2O)_6^{3+}$ absorbs yellow-green light, a solution of it is violet.

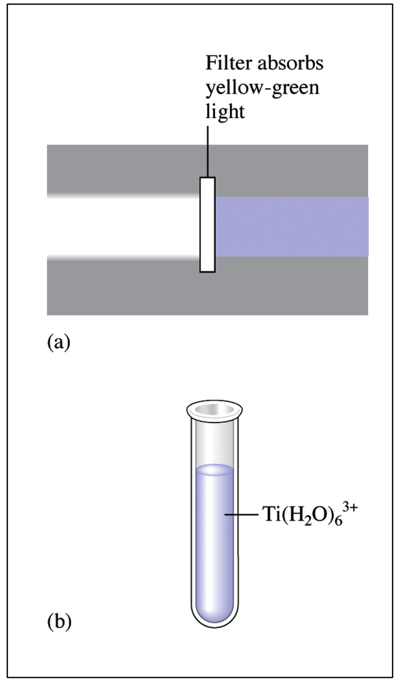


TABLE 21.16 Approximate Relationship of Wavelength of Visible Light Absorbed to Color Observed

Absorbed Wavelength in nm (Color)	Observed Color
400 (violet)	Greenish yellow
450 (blue)	Yellow
490 (blue-green)	Red
570 (yellow-green)	Violet
580 (yellow)	Dark blue
600 (orange)	Blue
650 (red)	Green

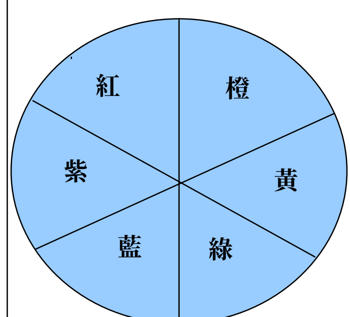


Figure 21.25: The complex ion $Ti(H_2O)_6^{3+}$ can absorb visible light in the yellow-green region to transfer the lone d electron from the t_{2g} to the e_g set.

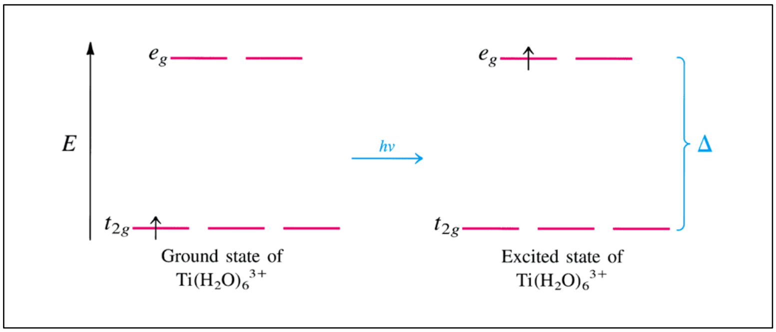


TABLE 21.17
Several Octahedral Complexes of Cr^{3+} and Their Colors

Isomer	Color
$[Cr(H_2O)_6]Cl_3$	Violet
$[Cr(H_2O)_5Cl]Cl_2$	Blue-green
$[Cr(H_2O)_4Cl_2]Cl$	Green
$[Cr(NH_3)_6]Cl_3$	Yellow
$[Cr(NH_3)_5Cl]Cl_2$	Purple
$[Cr(NH_3)_4Cl_2]Cl$	Violet

Solutions of $[Cr(NH_3)_6]Cl_3$ (yellow) and $[Cr(NH_3)_5Cl]Cl_2$ (purple)

Other Coordination Geometries

Figure 21.26: (a) Tetrahedral and octahedral arrangements of ligands shown inscribed in cubes.(b) The orientations of the 3*d* orbitals relative to the tetrahedral set of point charges.

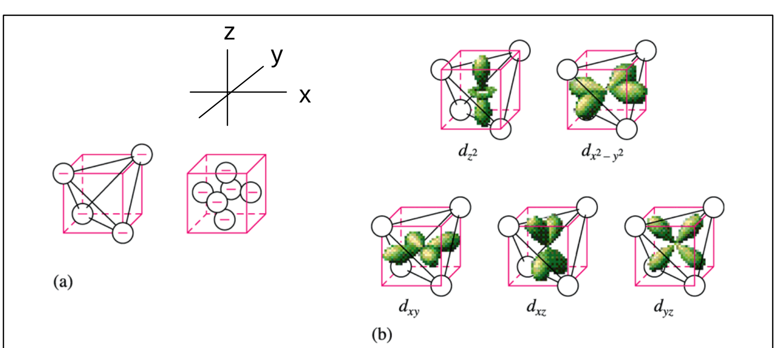
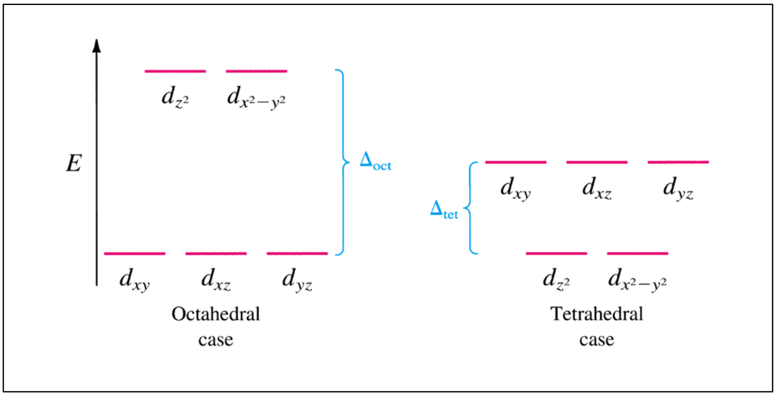
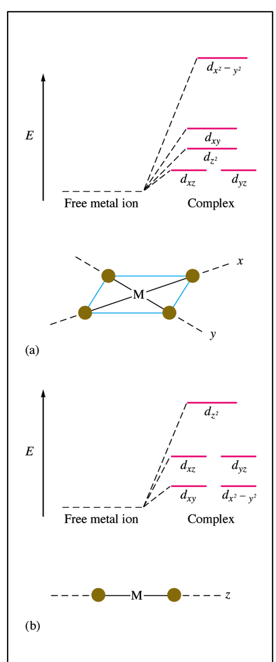


Figure 21.27: The crystal field diagrams for octahedral and tetrahedral complexes.



Td complexes **通常為** weak-field; $\Delta_{tet} = 4/9\ \Delta_{oct}$

Figure 21.28: (a) The crystal field diagram for a square planar complex oriented in the *xy* plane with ligands along the *x* and *y* axes.
(b) The crystal field diagram for a linear complex where the ligands lie along the *z* axis.



21.7 The Biologic Importance of Coordination Complexes

TABLE 21.18 The First-Row Transition Metals and Their Biologic Significance

First-Row Transition Metal	Biologic Function(s)
Scandium	None known.
Titanium	None known.
Vanadium	None known in humans.
Chromium	Assists insulin in the control of blood sugar; may also be involved in the control of cholesterol.
Manganese	Necessary for a number of enzymatic reactions.
Iron	Component of hemoglobin and myoglobin; involved in the electron-transport chain.
Cobalt	Component of vitamin B_{12}, which is essential for the metabolism of carbohydrates, fats, and proteins.
Nickel	Component of the enzymes urease and hydrogenase.
Copper	Component of several enzymes; assists in iron storage; involved in the production of color pigments of hair, skin, and eyes.
Zinc	Component of insulin and many enzymes.

Figure 21.29: The heme (原血紅素) complex, in which an Fe^{2+} ion is coordinated to four nitrogen atoms of a planar porphyrin ligand.

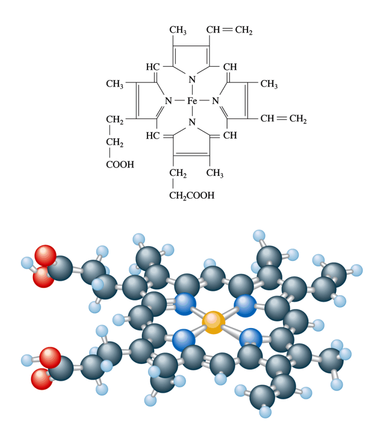


Figure 21.30: Chlorophyll (葉綠素)is a porphyrin complex of Mg^{2+}. There are two similar forms of chlorophyll, one of which is shown here.

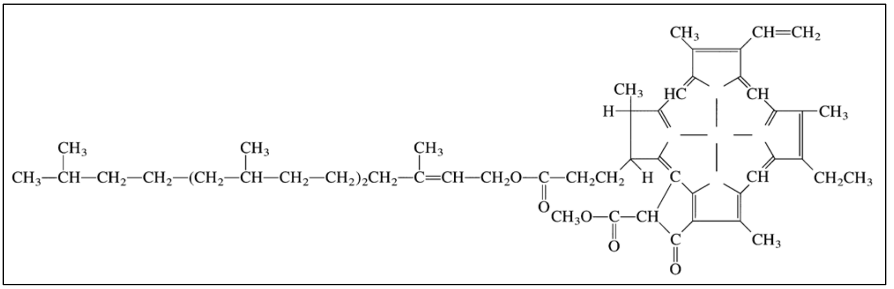


Figure 21.31: A representation of the myoglobin(肌紅蛋白) molecule.

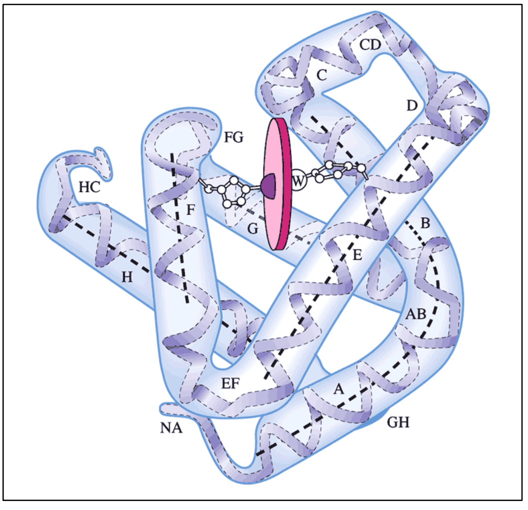


Figure 21.32: A representation of the hemoglobin (血紅素) structure.

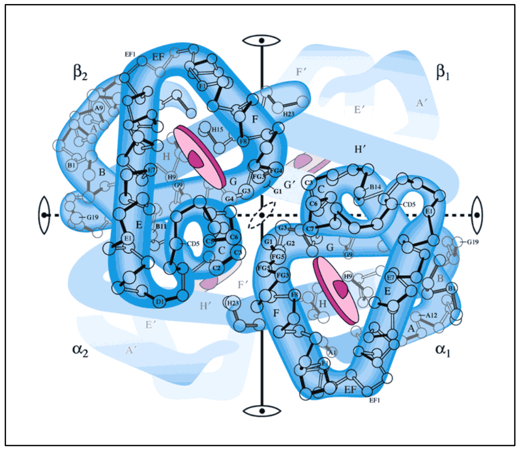
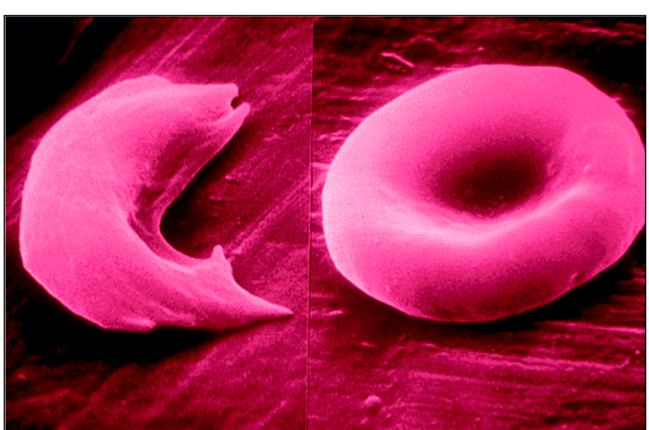


Figure 21.33: A normal red blood cell (right) and a sickle cell (left), both magnified 18,000 times.



21.8 Metallurgy and Iron and Steel Production

TABLE 21.19 Common Minerals Found in Ores

Anion	Examples
None (free metal)	Au, Ag, Pt, Pd, Rh, Ir, Ru
Oxide	Fe_2O_3 (hematite)
	Fe_3O_4 (magnetite)
	Al_2O_3 (bauxite)
	SnO_2 (cassiterite)
Sulfide	PbS (galena)
	ZnS (sphalerite)
	FeS_2 (pyrite)
	HgS (cinnabar)
	Cu_2S (chalcocite)
Chloride	NaCl (rock salt)
	KCl (sylvite)
	$KCl \cdot MgCl_2$ (carnalite)
Carbonate	$FeCO_3$ (siderite)
	$CaCO_3$ (limestone)
	$MgCO_3$ (magnesite)
	$MgCO_3 \cdot CaCO_3$ (dolomite)
Sulfate	$CaSO_4 \cdot 2H_2O$ (gypsum)
	$BaSO_4$ (barite)
Silicate	$Be_3Al_2Si_6O_{18}$ (beryl)
	$Al_2(Si_2O_8)(OH)_4$ (kaolinite)
	$LiAl(SiO_3)_2$ (spondumene)

Figure 21.34: A schematic diagram of a cyclone separator(氣旋分離器).

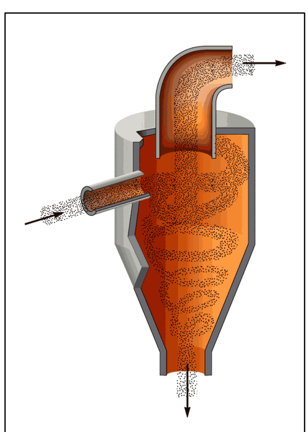


Figure 21.35: A schematic representation of zone refining.

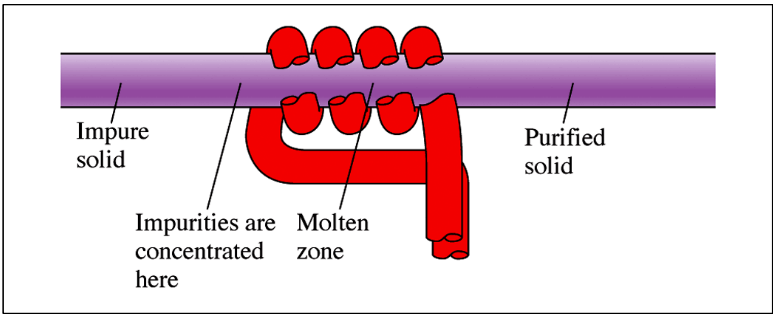


TABLE 21.20 **Examples of Methods for Recovery of Metal Ions from Leaching Solutions**

Method		Examples
Precipitation of a salt		$Cu^{2+}(aq) + S^{2-}(aq) \longrightarrow CuS(s)$
		$Cu^{+}(aq) + HCN(aq) \longrightarrow CuCN(s) + H^{+}(aq)$
Reduction	Chemical	$Au^{+}(aq) + Fe^{2+}(aq) \longrightarrow Au(s) + Fe^{3+}(aq)$
		$Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$
		$Ni^{2+}(aq) + H_2(g) \longrightarrow Ni(s) + 2H^{+}(aq)$
	Electrolytic	$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$
		$Al^{3+}(aq) + 3e^{-} \longrightarrow Al(s)$
Reduction plus precipitation		$2Cu^{2+}(aq) + 2Cl^{-}(aq) + H_2SO_3(aq) + H_2O(l) \longrightarrow 2CuCl(s) + 3H^{+}(aq) + HSO_4^{-}(aq)$

Figure 21.36: The blast furnace used in the production of iron.

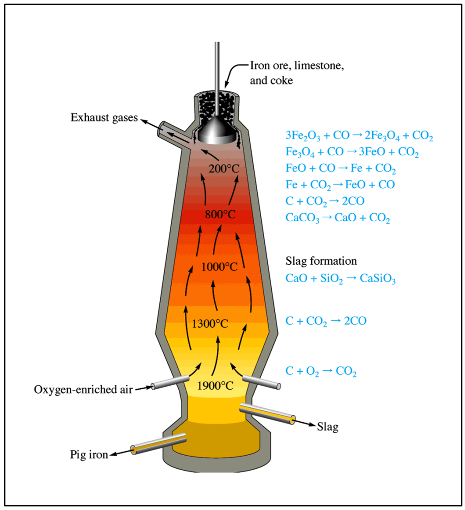


Figure 21.37: A schematic diagram of the open hearth process for steelmaking.

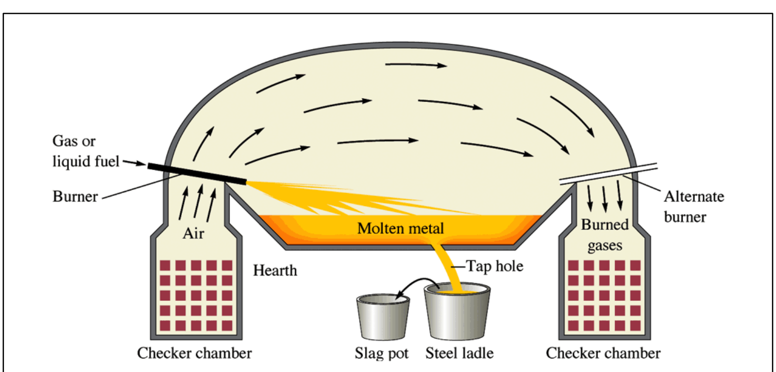


Figure 21.38: The basic oxygen process for steelmaking.

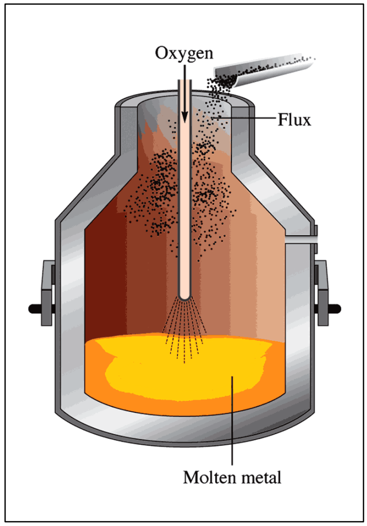


TABLE 21.21 Percent Composition and Uses of Various Types of Steel

Type of Steel	% Carbon	% Manganese	% Phosphorus	% Sulfur	% Silicon	% Nickel	% Chromium	% Other	Uses
Plain carbon	≤1.35	≤1.65	≤0.04	≤0.05	≤0.60	—	—	—	Sheet steel, tools
High-strength (low-alloy)	≤0.25	≤1.65	≤0.04	≤0.05	0.15–0.9	0.4–1	0.3–1.3	Cu (0.2–0.6) Sb (0.01–0.08) V (0.01–0.08)	Transportation equipment, structural beams
Alloy	≤1.00	≤3.50	≤0.04	≤0.05	0.15–2.0	0.25–10.0	0.25–4.0	Mo (0.08–4.0) V (0–0.2) W (0–18) Co (0–5)	Automobile and aircraft engine parts
Stainless	0.03–1.2	1.0–10	0.04–0.06	≤0.03	1–3	1–22	4.0–27	—	Engine parts, steam turbine parts, kitchen utensils
Silicon	—	—	—	—	0.5–5.0	—	—	—	Electric motors and transformers