Petrucci's General Chemistry

PRINCIPLES AND MODERN APPLICATIONS

Twelfth Edition

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Complex Ions and Coordination Compounds

24

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24-1 Werner's Theory of Coordination Compounds: An Overview

▲ FIGURE 24-1
Two coordination compounds

▲ Alfred Werner (1866-1919)

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

Complex cation

$[CoCl_4(NH_3)_2]^-$

Complex anion

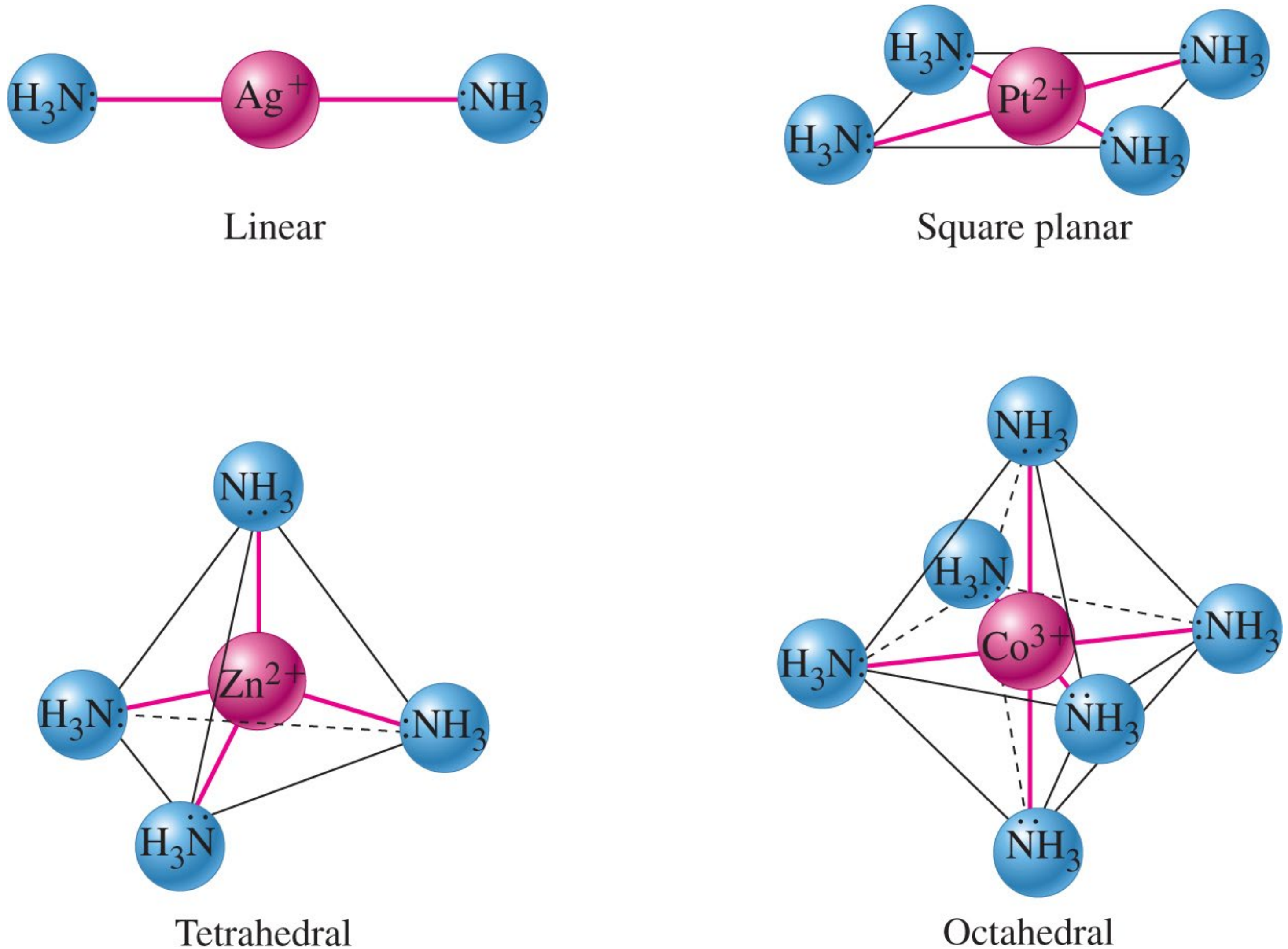
$[CoCl_3(NH_3)_3]$

Neutral complex

$K_4[Fe(CN)_6]$

Coordination compound

Table 24.1	Some Common Coordination Numbers of Metal Ions
Cu^+	2, 4
Ag^+	2
Au^+	2, 4
Fe^{2+}	6
Co^{2+}	4, 6
Ni^{2+}	4, 6
Cu^{2+}	4, 6
Zn^{2+}	4
Pt^{2+}	4
Al^{3+}	4, 6
Sc^{3+}	6
Cr^{3+}	6
Fe^{3+}	6
Co^{3+}	6
Au^{3+}	4
Pt^{4+}	6



▲ FIGURE 24-2

Structures of some complex ions

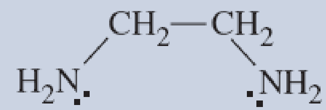
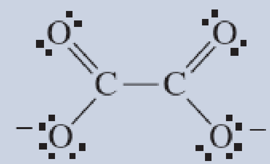
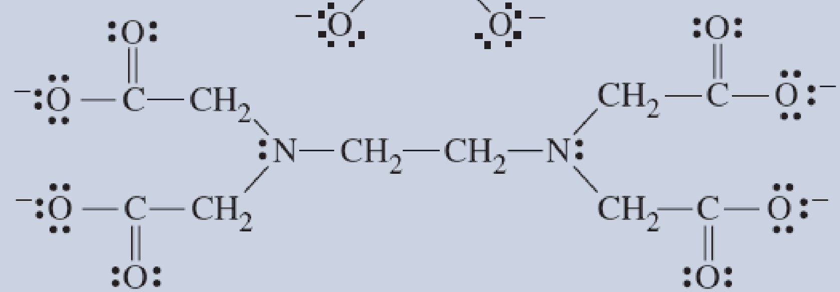
24-2 Ligands

Table 24.2 Some Common Monodentate Ligands

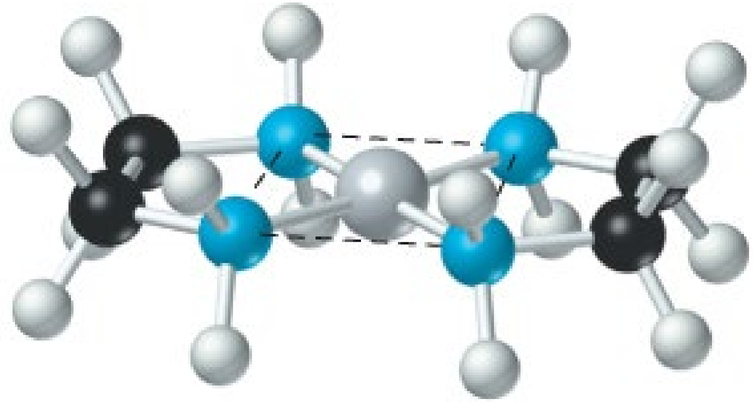
Formula	Name as Ligand	Formula	Name as Ligand[a]	Formula	Name as Ligand
Neutral molecules		Anions		Anions	
H_2O	Aqua	F^-	Fluorido	SO_4^{2-}	Sulfato
NH_3	Ammine	Cl^-	Chlorido	$S_2O_3^{2-}$	Thiosulfato
CO	Carbonyl	Br^-	Bromido	NO_2^-	Nitrito-*N*-[b]
NO	Oxidonitrogen	I^-	Iodido	ONO^-	Nitrito-*O*-[b]
CH_3NH_2	Methanamine	O^{2-}	Oxido	SCN^-	Thiocyanato-*S*-[c]
C_5H_5N	Pyridine	OH^-	Hydroxido	NCS^-	Thiocyanato-*N*-[c]
		CN^-	Cyanido		

[a] Before 2005, these ligands were named as follows: F^-, fluoro; Cl^-, chloro; Br^-, bromo; I^-, iodo; O^{2-}, oxo; OH^-, hydroxo; CN^-, cyano.
[b] If the nitrite ion is attached through the N atom ($—NO_2$), the designation *nitrito-N-* is used; if attached through an O atom ($—ONO$), *nitrito-O-*.
[c] If the thiocyanate ion is attached through the S atom ($—SCN$), the name *thiocyanato-S-* is used; if attachment is through the N atom ($—NCS$), *thiocyanato-N-*.

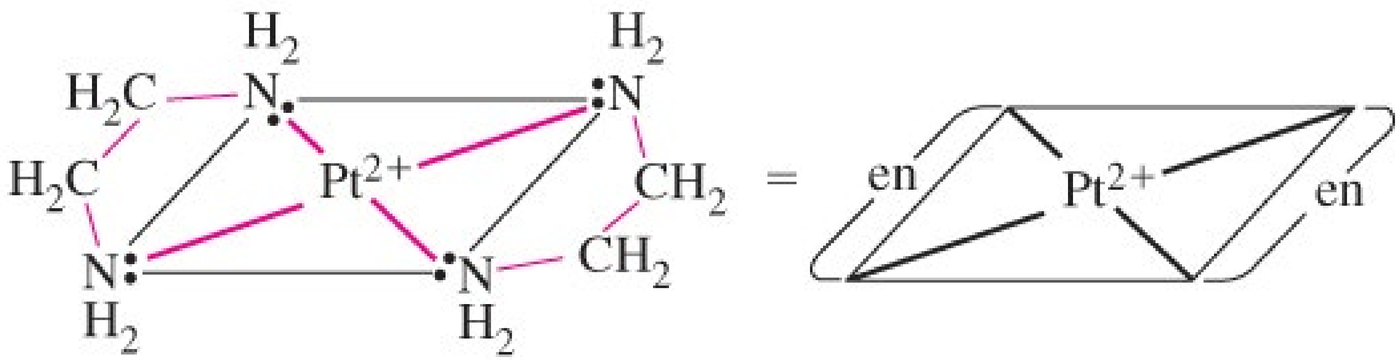
Table 24.3 Some Common Polydentate Ligands (Chelating Agents)

Abbreviation	Name	Formula
en	Ethylenediamine	
ox^{2-} [a]	Oxalato	
$EDTA^{4-}$ [b]	Ethylenediaminetetraacetato	

[a]Oxalic acid is a diprotic acid denoted H_2ox. It is the ox^{2-} anion that binds as a bidentate ligand.
[b]Ethylenediaminetetraacetic acid, a tetraprotic acid, is denoted H_4EDTA.



(a)



(b)

▲ FIGURE 24-3
Three representations of the chelate $[Pt(en)_2]^{2+}$

24-3 Nomenclature

1) *Anions as ligands are named using the ending –o*

   –ide changes to–ido, –ite to –ito, and –ate to –ato.

2) *Neutral molecules generally carry the unmodified name*

3) *The number of ligands is denoted by a prefix*

   mono, di, tri, tetra, penta, hexa

4) *Ligands are named first in alphabetical order followed by the name of the metal center. Oxidation state is denoted by a Roman numeral. Anions end the metal name in -ate*

5) *Formula is written with metal first, followed by the ligand symbols in alphabetical order*

6) *Cations come first, followed by anions*

Table 24.4		Names for Some Metals in Complex Anions
Iron	$\longrightarrow$	Ferrate
Copper	$\longrightarrow$	Cuprate
Tin	$\longrightarrow$	Stannate
Silver	$\longrightarrow$	Argentate
Lead	$\longrightarrow$	Plumbate
Gold	$\longrightarrow$	Aurate

24-4 Isomerism

Ionization Isomerism

$[Cr(NH_3)_5SO_4]Cl$

Pentamminesulfatochromium (III) chloride

$[CrCl(NH_3)_5]SO_4$

Pentamminechloridochromiium(III) sulfate

Coordination Isomerism

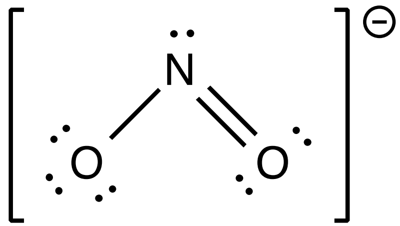
$[Co(NH_3)_6][Cr(CN)_6]$

Hexaamminecobalt(III) hexacyanidochromate(III)

$[Cr(NH_3)_6][Co(CN)_6]$

Hexaamminechromium(III) hexacyanidocobaltate(III)

Linkage Isomerism



$[Co(NO_2)(NH_3)_5]^{2+}$

Pentaamminenitrito-*N*-cobalt(III) ion

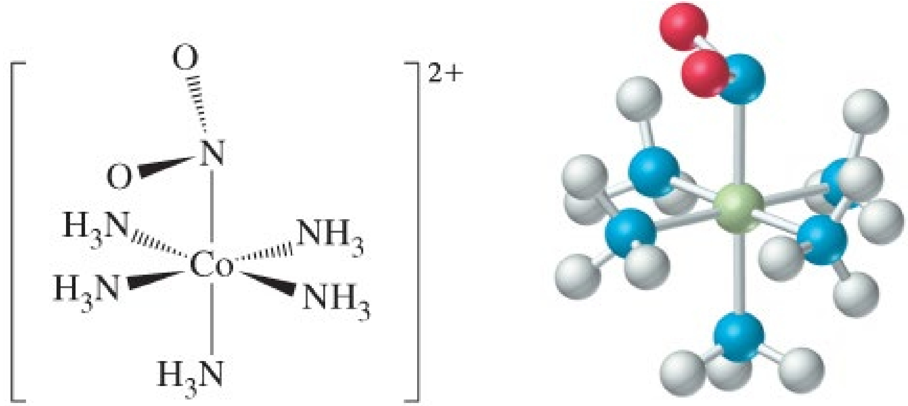
$[Co(NH_3)_5(ONO)]^{2+}$

Pentaamminenitrito-*O*-cobalt(III) ion

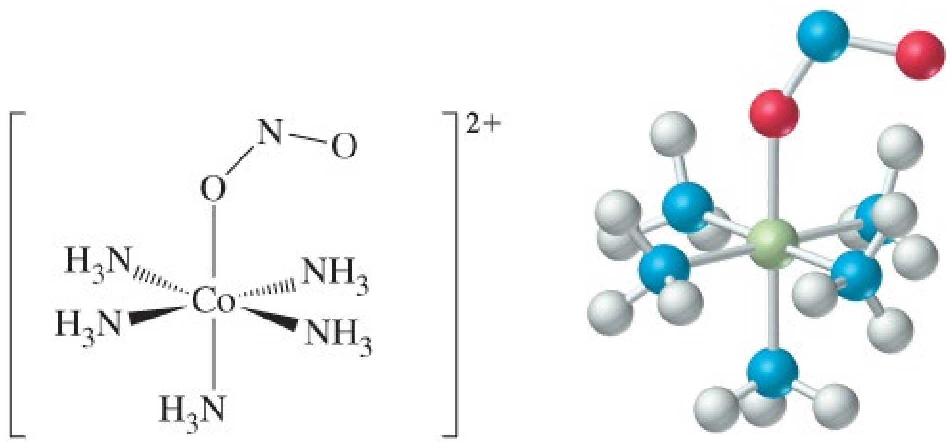
Geometric Isomerism

$[PtCl_2(NH_3)_2]$

cis-diamminedichloridoplatinum(II)
or
trans-diamminedichloridoplatinum(II)



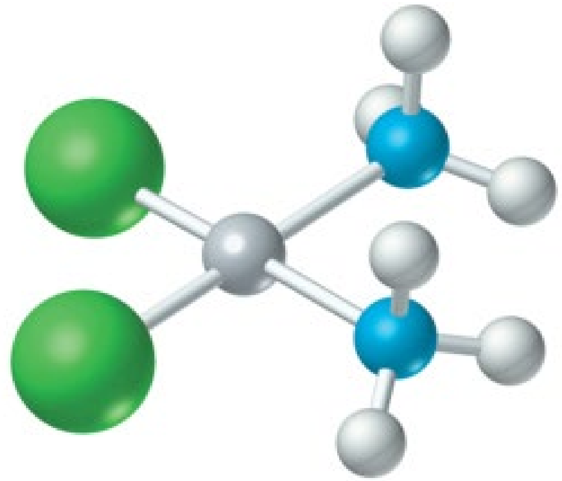
(a) $[Co(NH_3)_5NO_2]^{2+}$



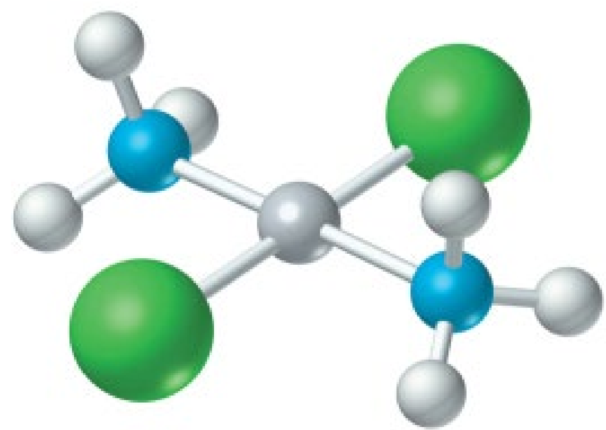
(b) $[Co(NH_3)_5(ONO)]^{2+}$

▲ FIGURE 24-4

Linkage isomerism-illustrated

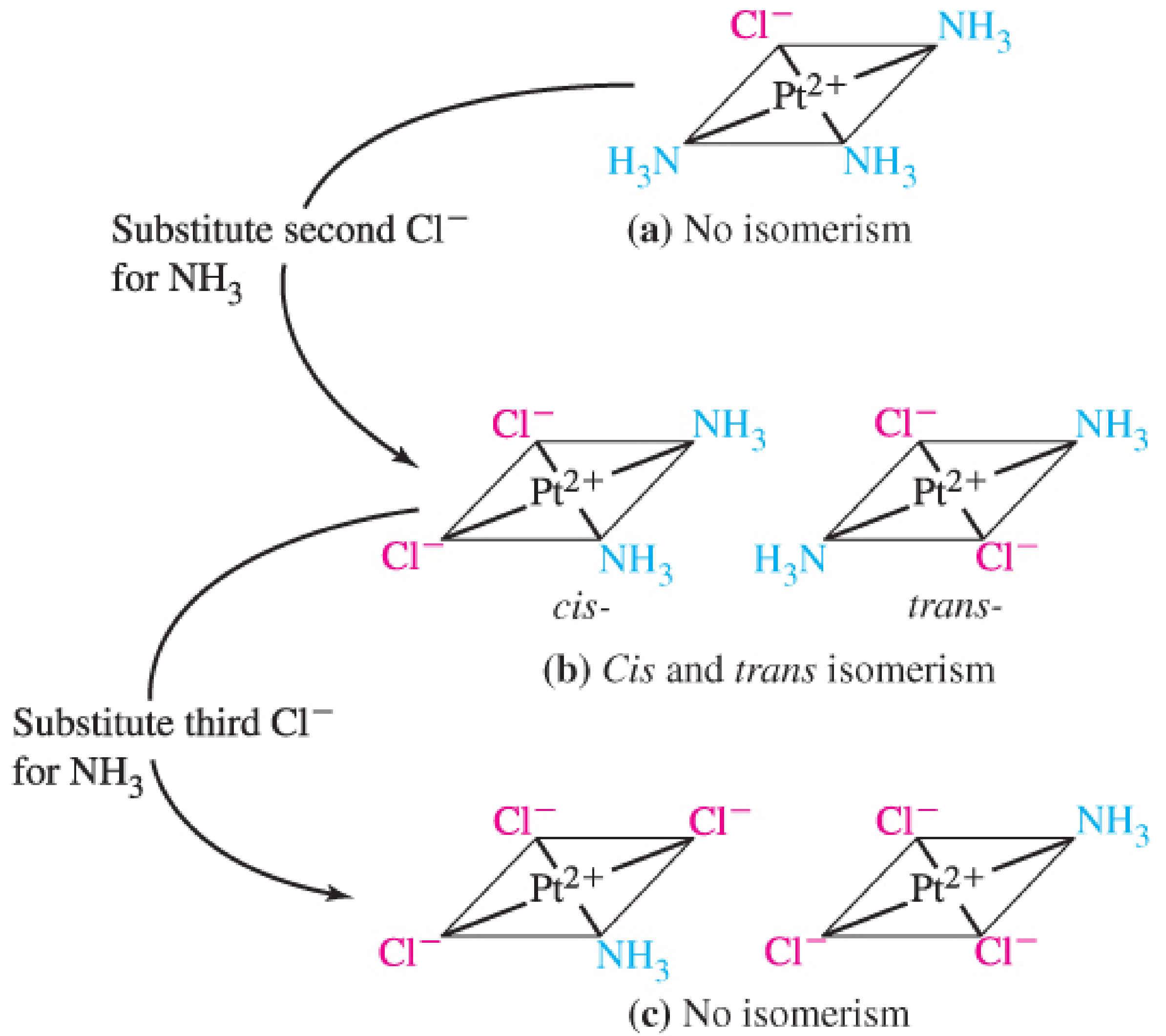


cis-$[PtCl_2(NH_3)_2]$



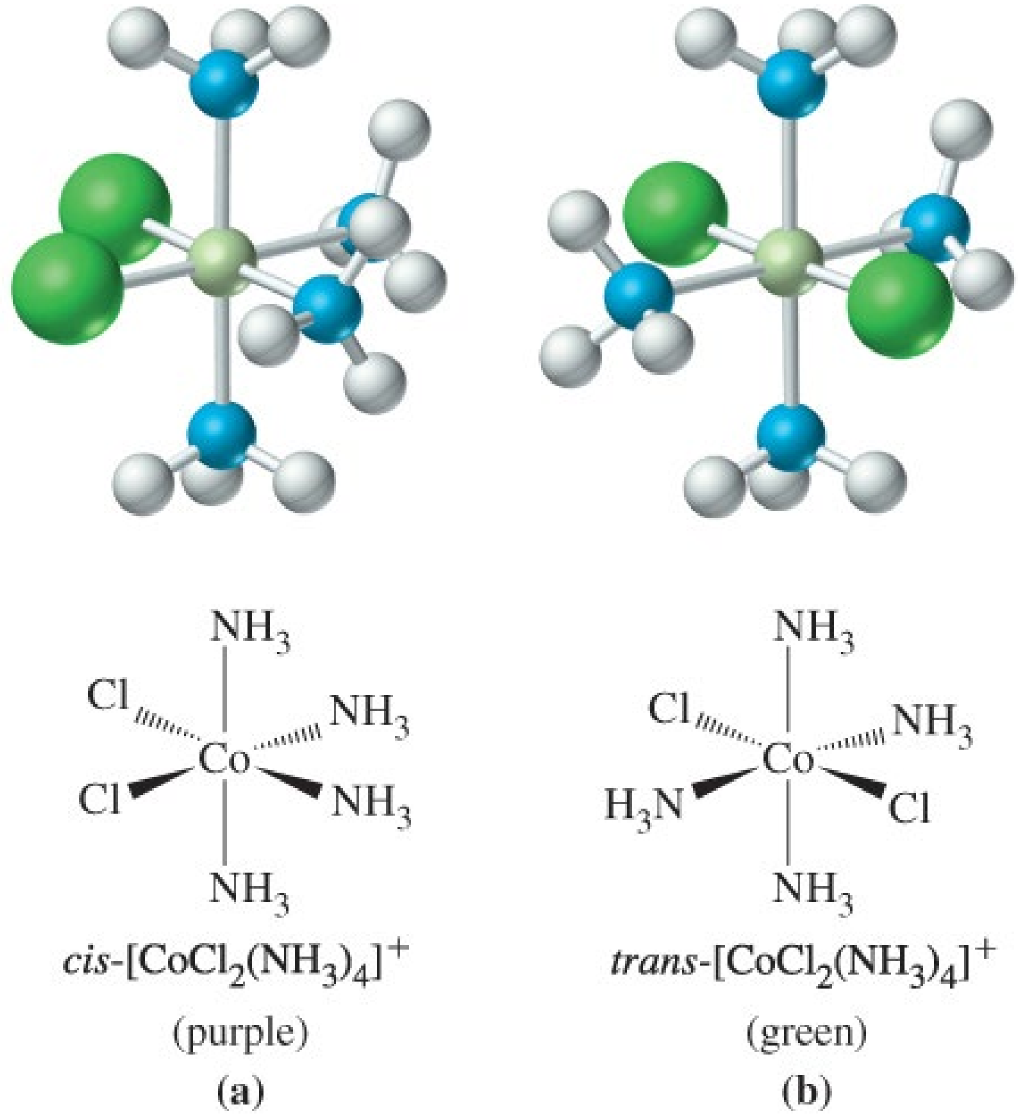
trans-$[PtCl_2(NH_3)_2]$

▲ The geometric isomers of $[PtCl_2(NH_3)_2]$



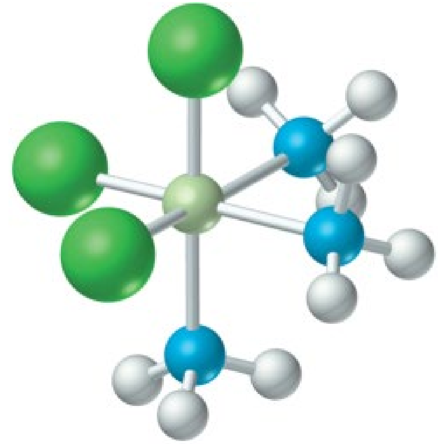
▲ FIGURE 24-5

Geometric isomerism-illustrated

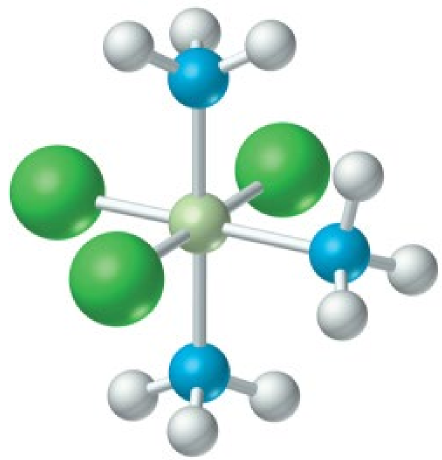


▲ FIGURE 24-6

***Cis* and *trans* isomers of an octahedral complex**



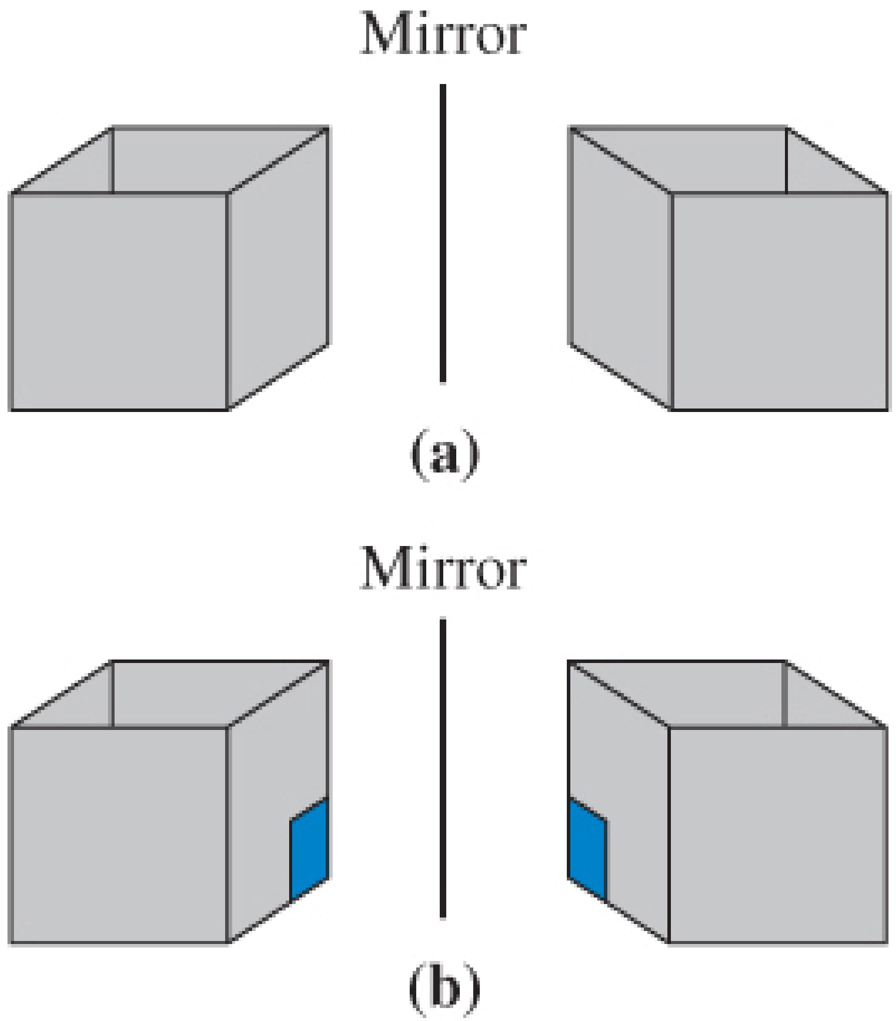
fac-$[CoCl_3(NH_3)_3]$



mer-$[CoCl_3(NH_3)_3]$

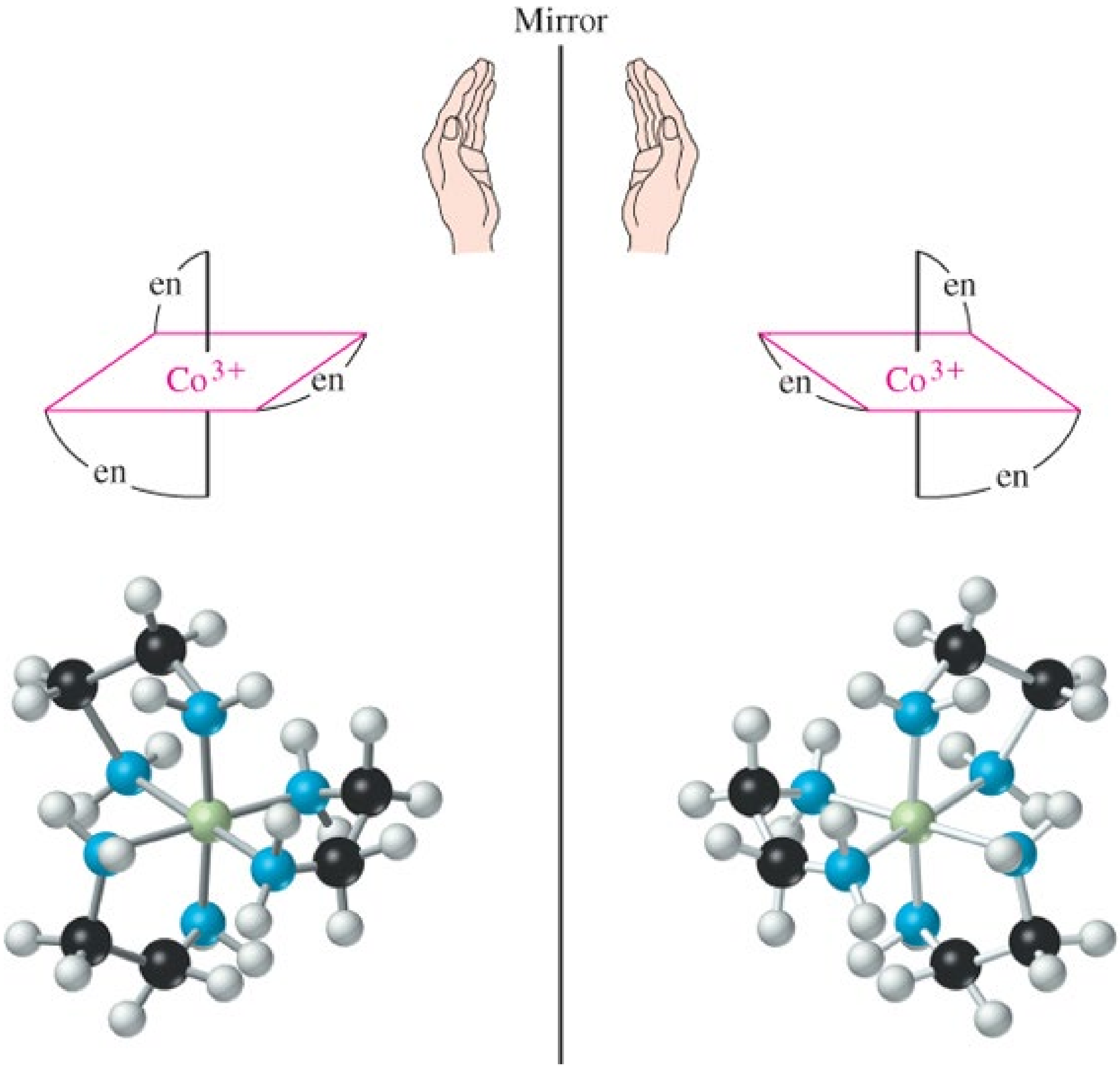
▲ The geometric isomers of $[CoCl_3(NH_3)_3]$

Optical Isomerism

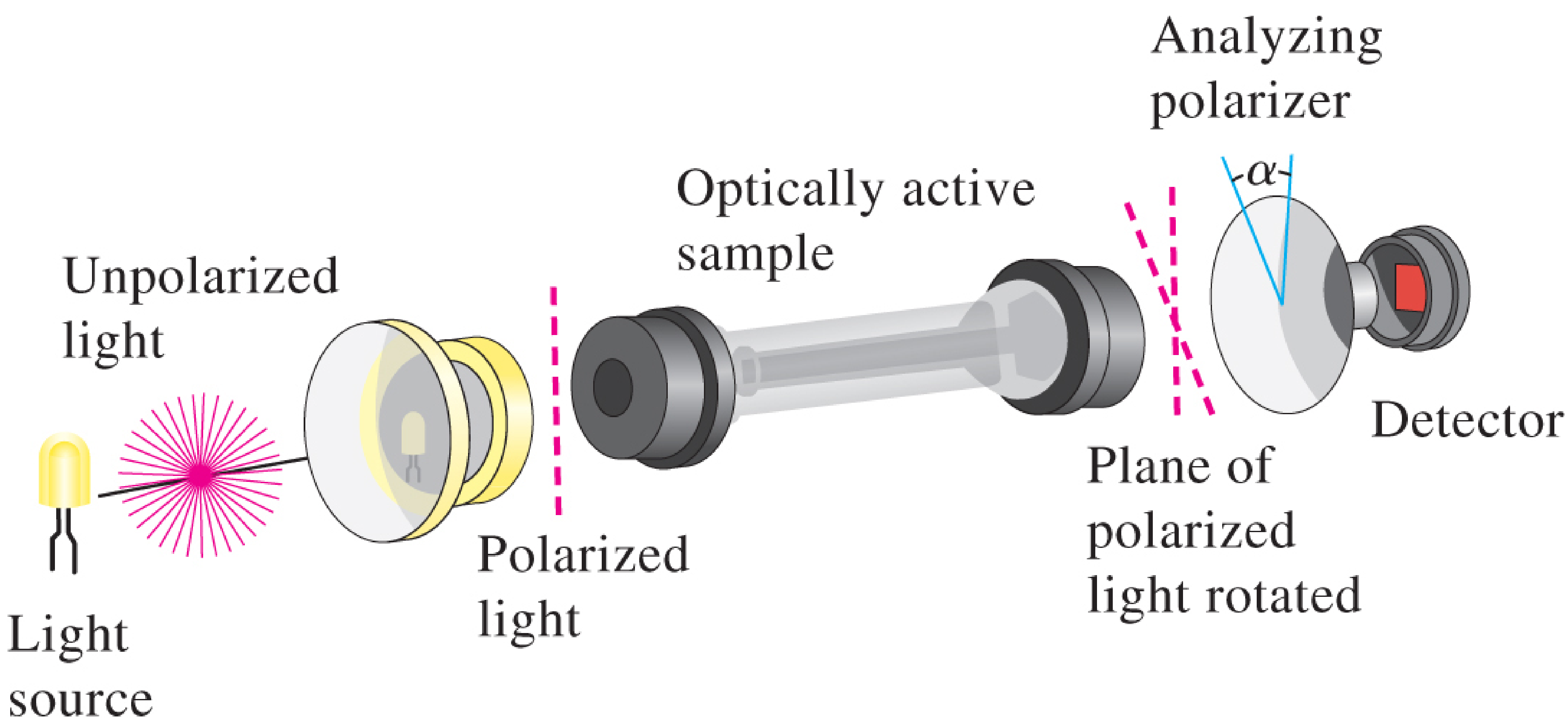


▲ Figure 24-7

Superimposable and nonsuperimposable objects–an open-top box

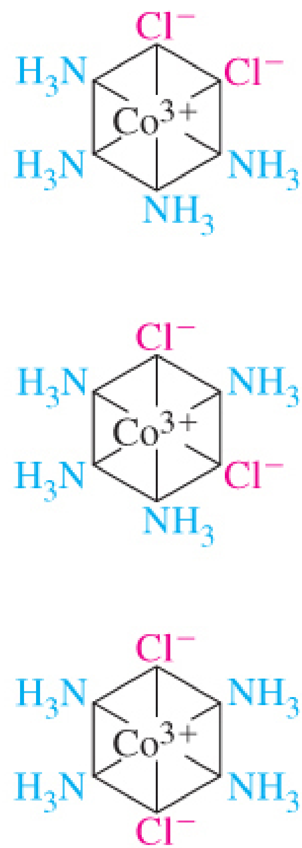


▲ FIGURE 24-8
Optical Isomers



▲ FIGURE 24-9
Optical Activity

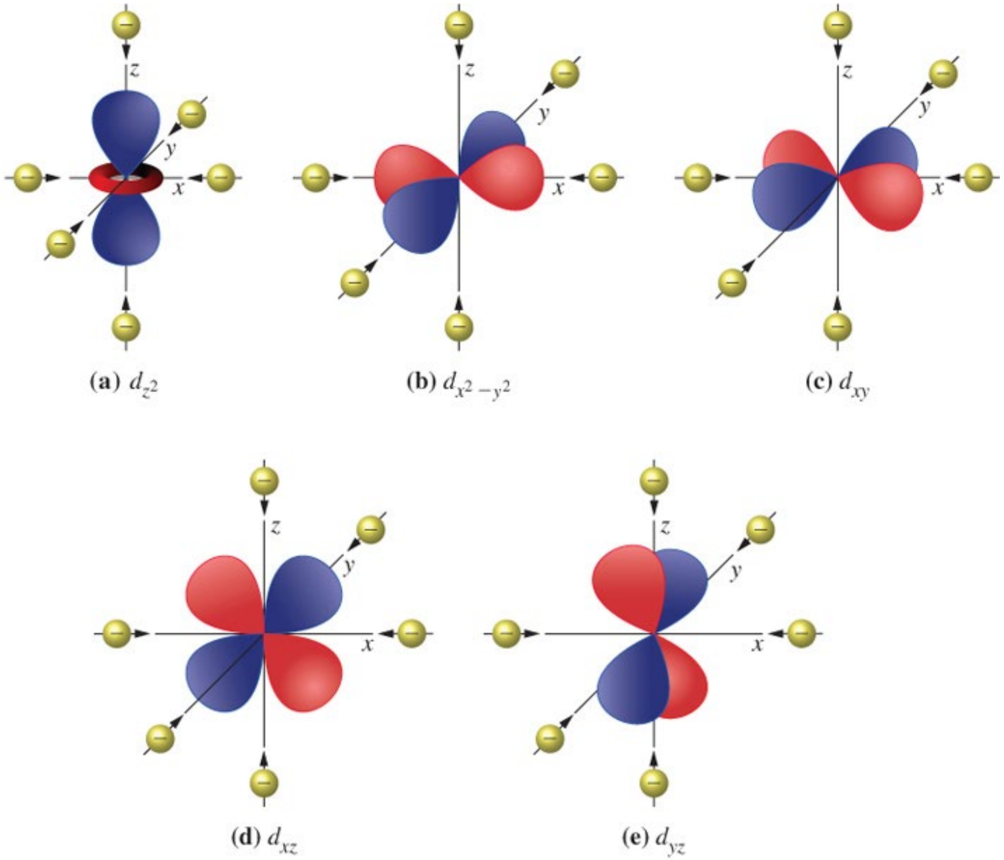
Isomerism and Werner's Theory



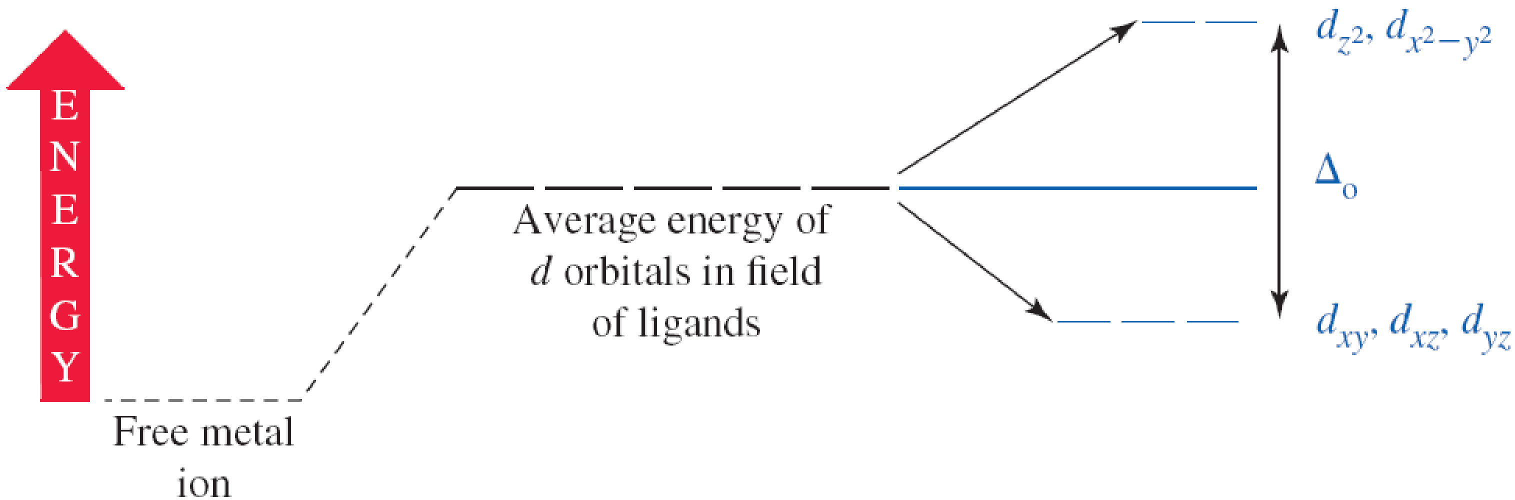
▲ FIGURE 24-10

Hypothetical strucutres for $[CoCl_2(NH_3)_4]^+$

24-5 Bonding in Complex Ions: Crystal Field Theory

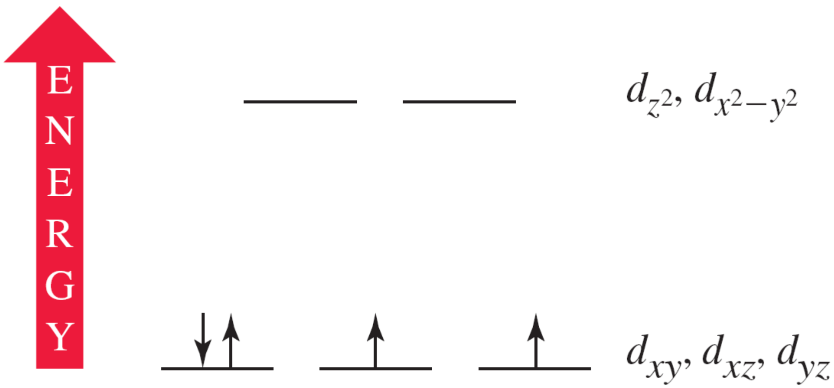


▲ FIGURE 24-1
Approach of six anions to a metal ion to form a complex ion with octahedral structure

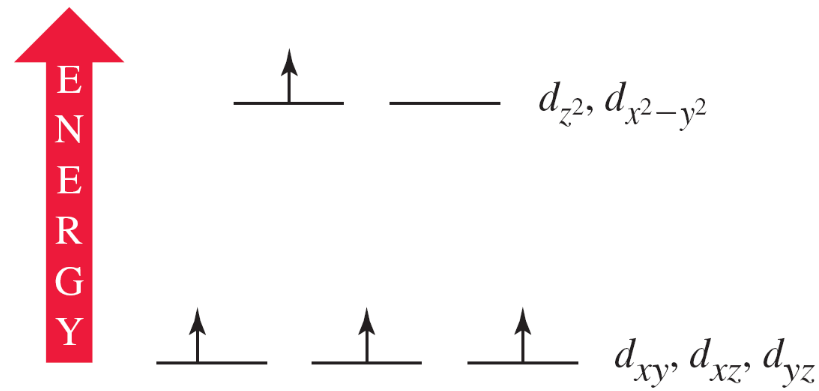


▲ FIGURE 24-12

Splitting of d energy levels in the formation of an octahedral complex ion



low spin



high spin

Strong field

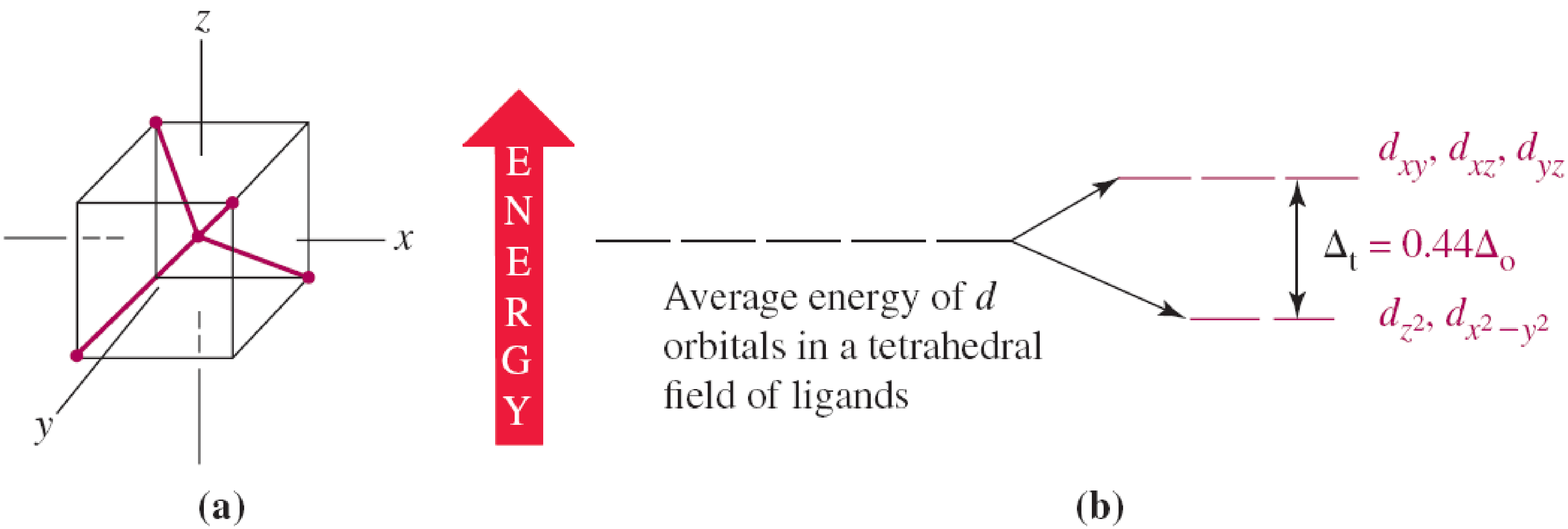
(large Δ_o)

$CN^- > NO_2^- >$ en $>$ py $\approx NH_3 > EDTA^{4-} > SCN^- > H_2O >$
$ONO^- >$ ox$^{2-} > OH^- > F^- > SCN^- > Cl^- > Br^- > I^-$

(small Δ_o)

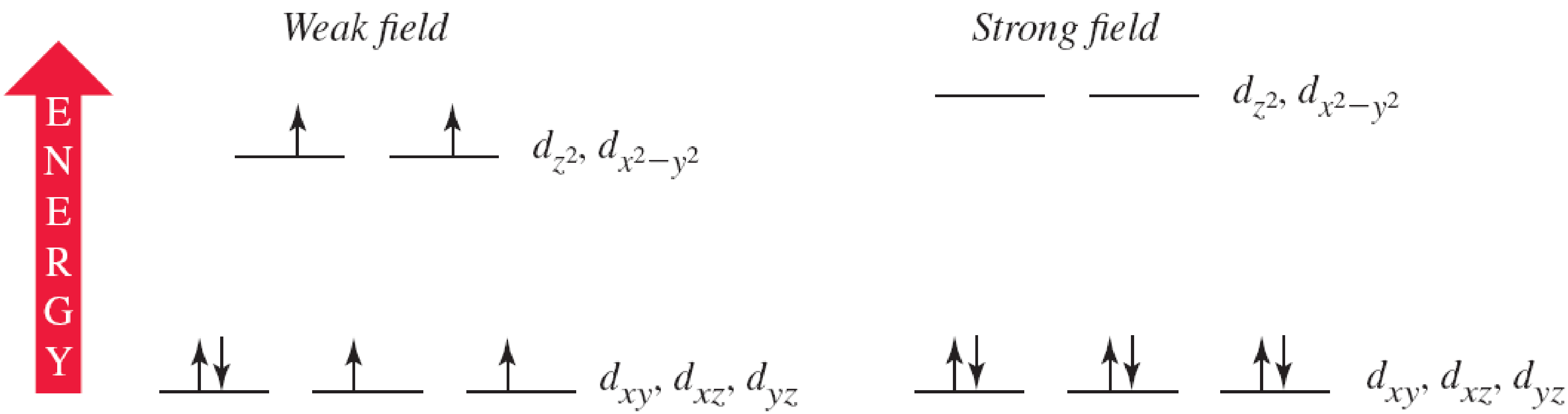
The red color indicates the donor atom.

Weak field



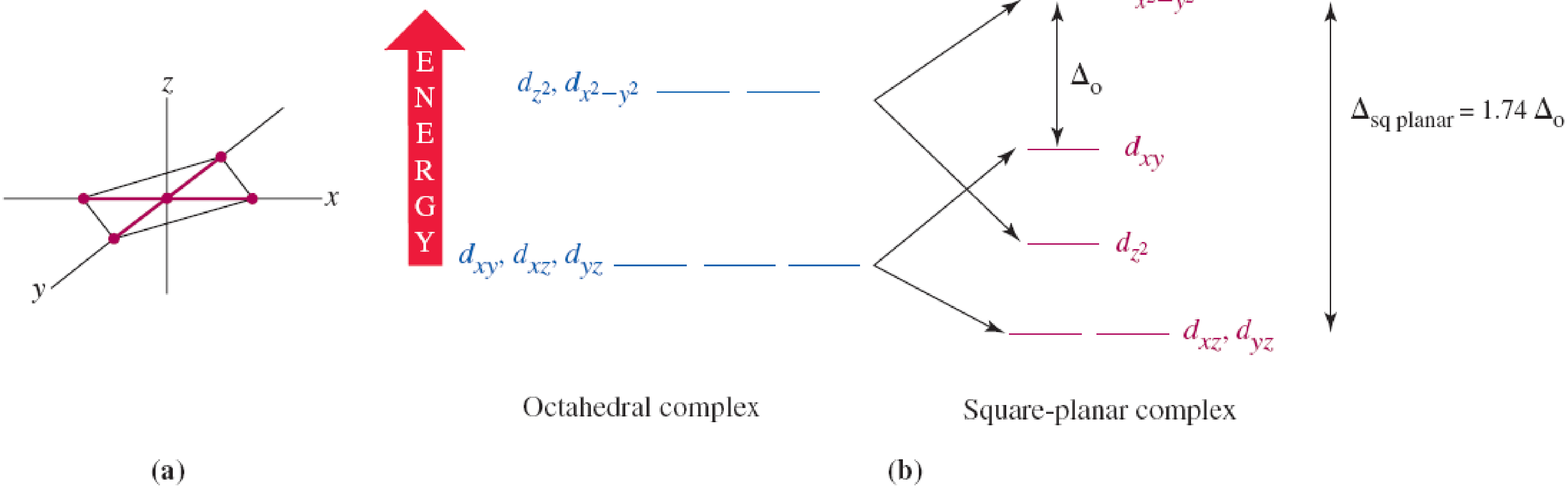
▲ FIGURE 24-13

Crystal field splitting in a tetrahedral complex ion



High-spin complex
$[CoF_6]^{3-}$
$\Delta_o < P$

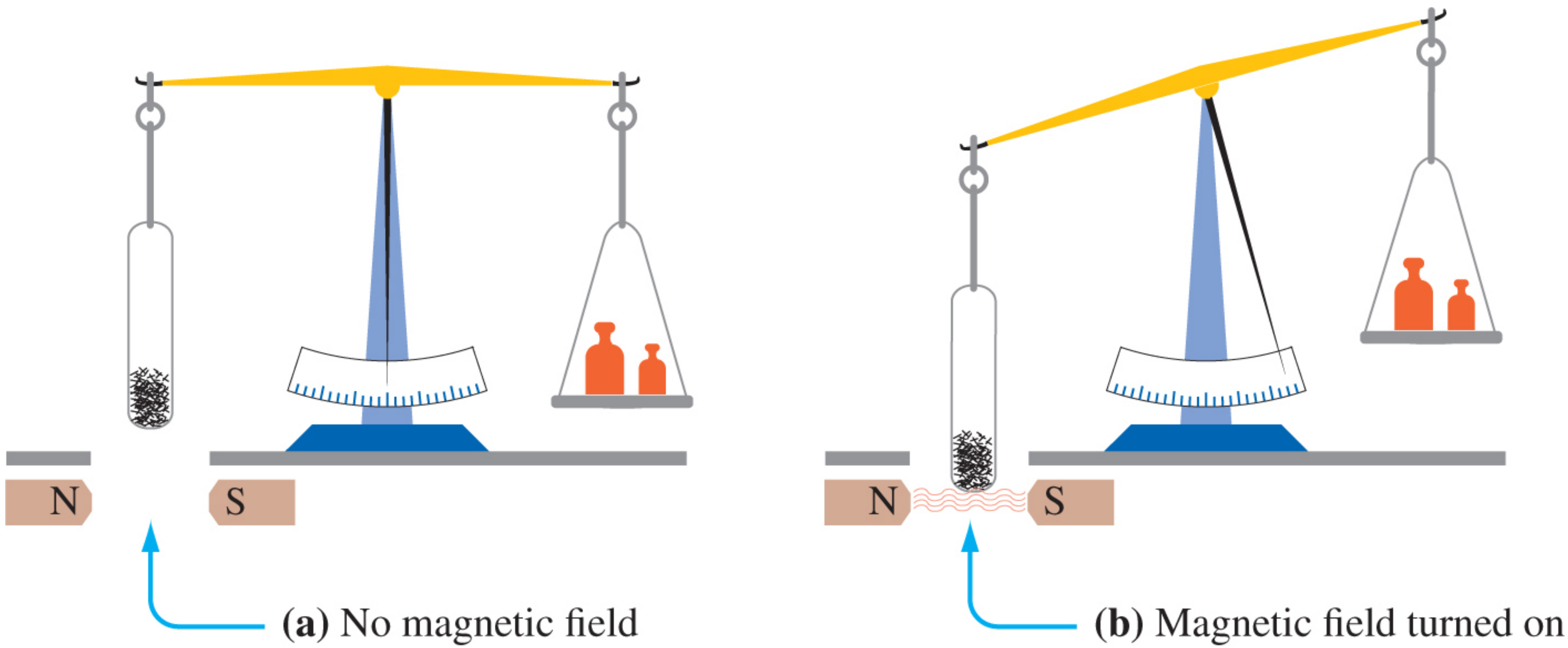
Low-spin complex
$[Co(NH_3)_6]^{3+}$
$\Delta_o > P$



▲ FIGURE 24-14

Comparison of crystal field splitting in a square-planar and an octahedral complex

24-6 Magnetic Properties of Coordination Compounds and Crystal Field Theory

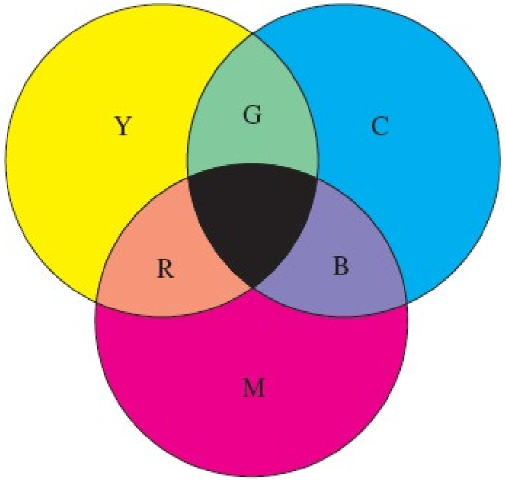


▲ FIGURE 24-15
Paramagnetism–illustrated

24-7 Color and the Colors of Complexes

Primary, Secondary and Complimentary Colors

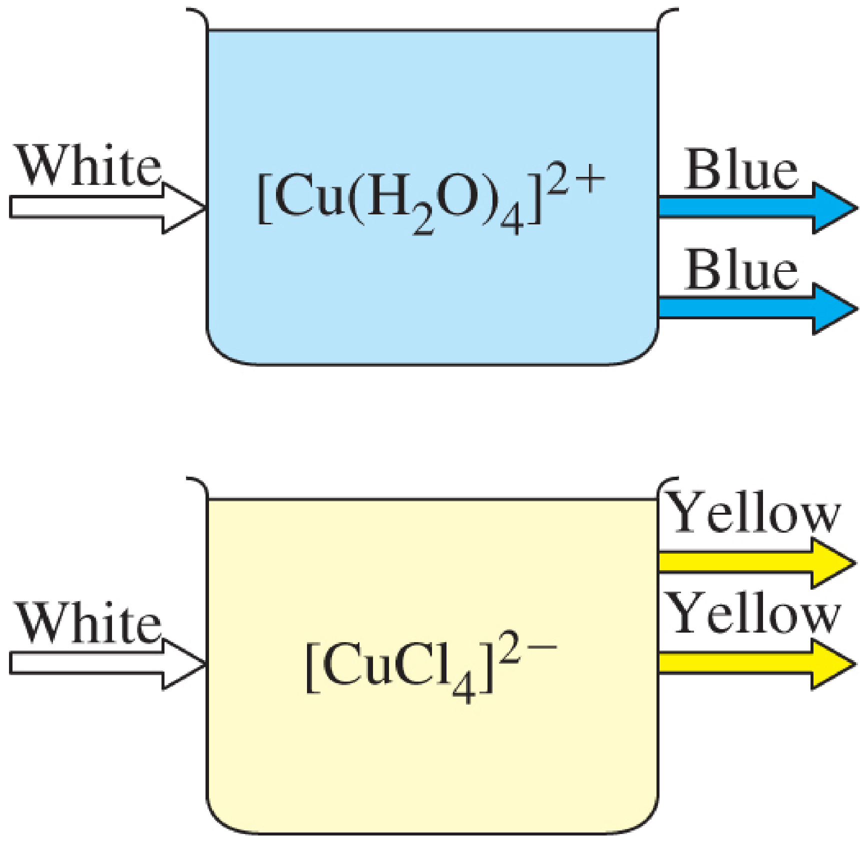
(a) Additive color mixing



(b) Subtractive color mixing

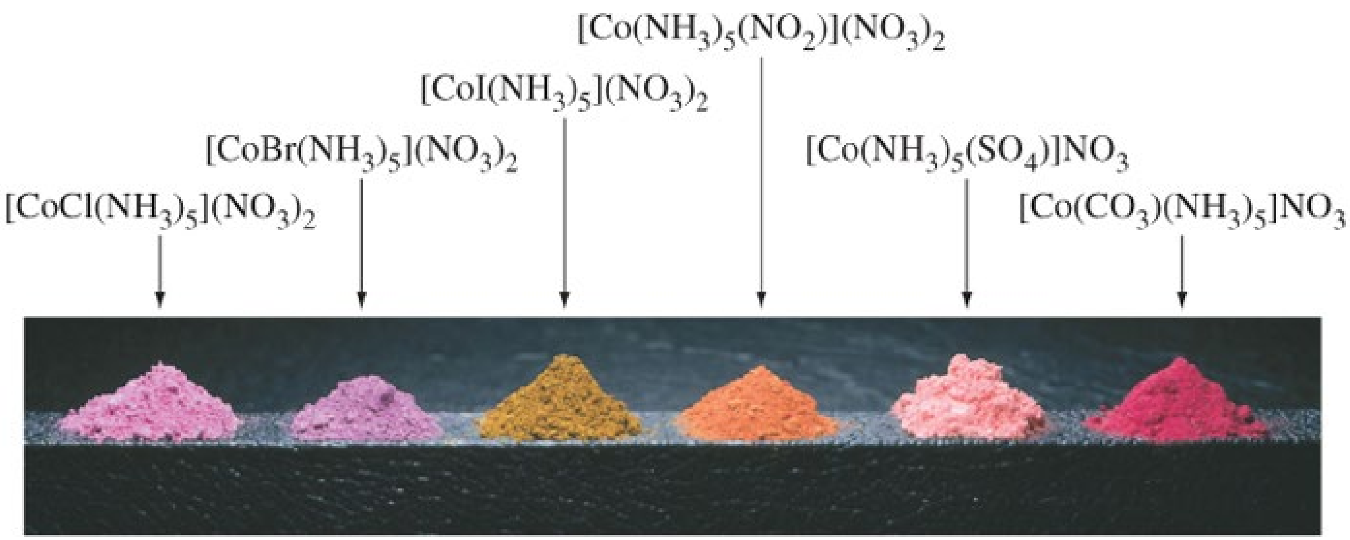
▲ FIGURE 24-16
The mixing of colors

Colored Solutions



▲ FIGURE 24-17
Light absorption and transmission

Table 24.5	Some Coordination Compounds of Cr^{3+} and Their Colors
Isomer	**Color**
$[Cr(H_2O)_6]Cl_3$	Violet
$[CrCl(H_2O)_5]Cl_2$	Blue-green
$[Cr(NH_3)_6]Cl_3$	Yellow
$[CrCl(NH_3)_5]Cl_2$	Purple



▲ FIGURE 24-18

Effects of ligands on the colors of coordination compounds

$$Zn^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons [Zn(NH_3)_4]^{2+}(aq) \tag{24.1}$$

$$K_f = \frac{[[Zn(NH_3)_4]]^{2+}}{[Zn^{2+}][NH_3]^4} = 4.1 \times 10^8 \tag{24.2}$$

The displacement occurs in a stepwise fashion:

$$[Zn(H_2O)_4]^{2+} + NH_3 \rightleftharpoons [Zn(H_2O)_3(NH_3)]^{2+} + H_2O \tag{24.3}$$

$$K_1 = \frac{[[Zn(H_2O)_3(NH_3)]^{2+}]}{[[Zn(H_2O)_4]^{2+}][NH_3]} = 4.1 \times 10^8 \tag{24.4}$$

$$[Zn(H_2O)_3(NH_3)]^{2+} + NH_3 \rightleftharpoons [Zn(H_2O)_2(NH_3)_2]^{2+} + H_2O \tag{24.5}$$

$$K_2 = \frac{[[Zn(H_2O)_2(NH_3)_2]^{2+}]}{[[Zn(H_2O)_3(NH_3)]^{2+}][NH_3]} = 2.1 \times 10^2 \tag{24.6}$$

$$Zn^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons [Zn(NH_3)_4]^{2+}(aq) \qquad (24.1)$$

$$K_f = \frac{[[Zn(NH_3)_4]]^{2+}}{[Zn^{2+}][NH_3]^4} = 4.1 \times 10^8 \qquad (24.2)$$

K_1 is often designated β_1 and is called the formation constant for $[Zn(H_2O)_3NH_3]^{2+}$

β_2 is the formation constant for $[Zn(H_2O)_2(NH_3)_2]^{2+}$, the sum of (23.3) and (23.4)

$$[Zn(H_2O)_4]^{2+} + 2\,NH_3 \rightleftharpoons [Zn(H_2O)_2(NH_3)_2]^{2+} + 2\,H_2O \qquad (24.7)$$

$$\beta_2 = \frac{[[Zn(H_2O)_2(NH_3)_2]^{2+}]}{[[Zn(H_2O)_4]^{2+}][NH_3]^2} = K_1 \times K_2 = 8.2 \times 10^4 \qquad (24.8)$$

$$Zn^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons [Zn(NH_3)_4]^{2+}(aq) \qquad (24.1)$$

$$K_f = \frac{[[Zn(NH_3)_4]]^{2+}}{[Zn^{2+}][NH_3]^4} = 4.1 \times 10^8 \qquad (24.2)$$

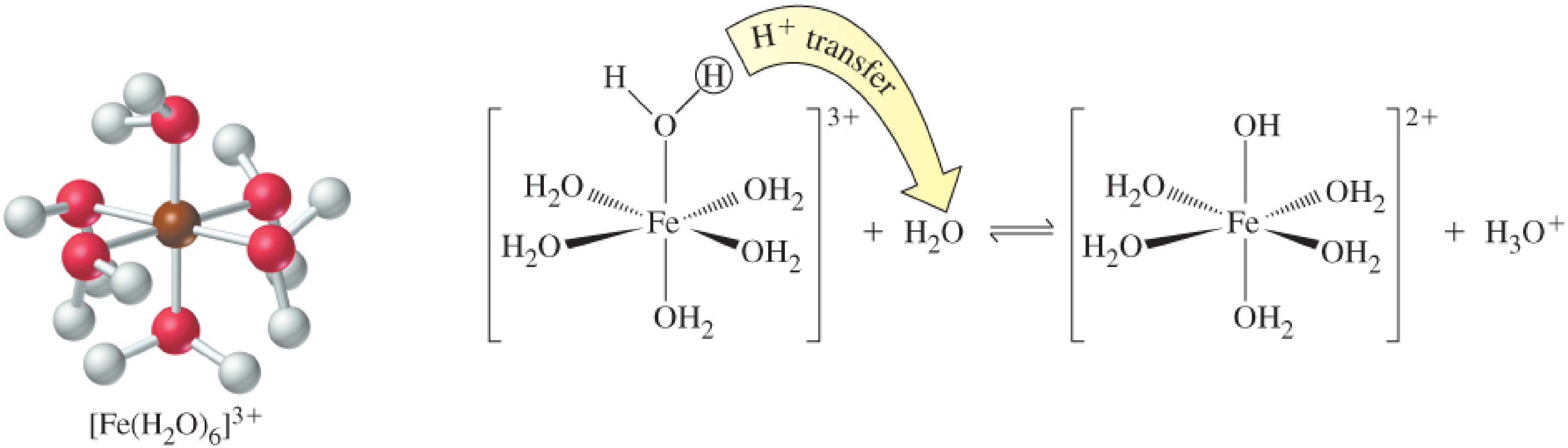
The formation constants for all four ions in the series are given by:

$[Zn(H_2O)_3NH_3]^{2+}$	$\beta_1 = K_1$
$[Zn(H_2O)_2(NH_3)_2]^{2+}$	$\beta_2 = K_1 \times K_2$
$[Zn(H_2O)_1(NH_3)_3]^{2+}$	$\beta_2 = K_1 \times K_2 \times K_3$
$[Zn(NH_3)_4]^{2+}$	$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$

Table 24.6 Stepwise and Overall Formation (Stability) Constants for Several Complex Ions							
Metal[a] Ion	Ligand	K_1	K_2	K_3	K_4	K_5	K_6	β_n (or K_f)[b]
Ag^+	NH_3	2.0×10^3	7.9×10^3					1.6×10^7
Zn^{2+}	NH_3	3.9×10^2	2.1×10^2	1.0×10^2	5.0×10^1			4.1×10^8
Cu^{2+}	NH_3	1.9×10^4	3.9×10^3	1.0×10^3	1.5×10^2			1.1×10^{13}
Ni^{2+}	NH_3	6.3×10^2	1.7×10^2	5.4×10^1	1.5×10^1	5.6	1.1	5.3×10^8
Cu^{2+}	en	5.2×10^{10}	2.0×10^9					1.0×10^{20}
Ni^{2+}	en	3.3×10^7	1.9×10^6	1.8×10^4				1.1×10^{18}
Ni^{2+}	EDTA	4.2×10^{18}						4.2×10^{18}

[a]In many tabulations in the chemical literature, formation-constant data are presented as logarithms: that is, $\log K_1$, $\log K_2, \ldots$, and $\log \beta_n$.
[b]The β_n listed is for the number of steps shown: e.g., for $[Ag(NH_3)_2]^+$, $\beta_2 = K_f = K_1 \times K_2$; for $[Ni(en)_3]^{2+}$, $\beta_3 = K_f = K_1 \times K_2 \times K_3$; and for $[Ni(EDTA)]^{2-}$, $\beta_1 = K_f = K_1$.

24-9 Acid-Base Reactions of Complex Ions



▲ FIGURE 24-19

Ionization of $[Fe(H_2O)_6]^{3+}$

24-10 Some Kinetic Considerations

$$[Cu(H_2O)_4]^{2+} + 4\,Cl^- \xrightleftharpoons{fast} [CuCl_4]^{2-} + 4\,H_2O$$

light blue

yellow in conc HCl

pale green in dil. HCl

$$[Cu(H_2O)_4]^{2+} + 4\,NH_3 \xrightleftharpoons{fast} [Cu(NH_3)_4]^{2+} + 4\,H_2O$$

light blue

deep blue

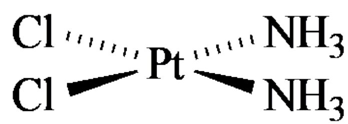
▲ FIGURE 24-20
Labile complex ions

$$\textit{trans}-[CrCl_2(H_2O)_4]^+ + 2\,H_2O \xrightleftharpoons{1\text{–}2\,d} [Cr(H_2O)_6]^{3+} + 2\,Cl^-$$

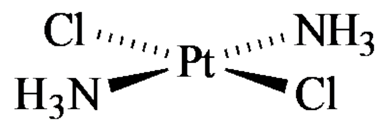
▲ FIGURE 24-2
Inert complex ions

24-11 Applications of Coordination Chemistry

Cisplatin: A Cancer-Fighting Drug

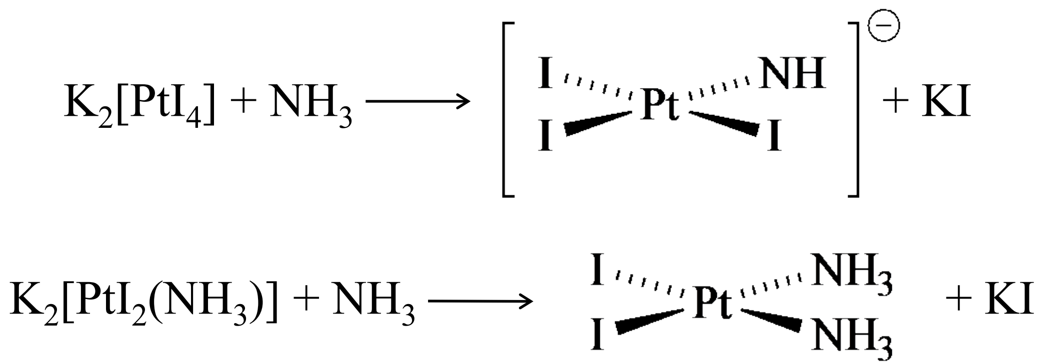


cis-$[PtCl_2(NH_3)_2]$
(cisplatin)



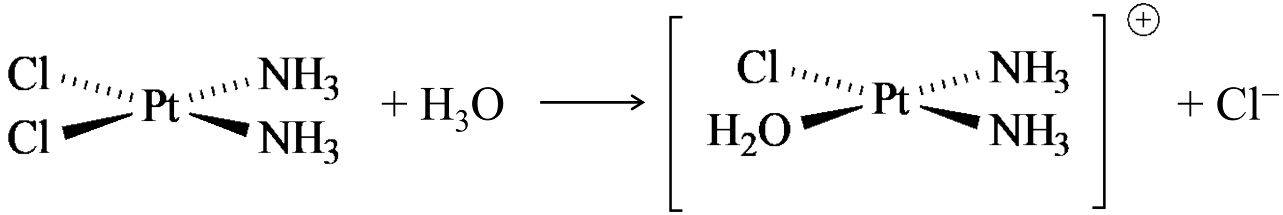
trans-$[PtCl_2(NH_3)_2]$
(transplatin)

$$K_2[PtCl_4] + 4KI \longrightarrow K_2[PtI_4] + 4\ KCl$$



treat with AgNO3 followed by KCl to obtain cisplatin

Cisplatin enters the cell by diffusion and hydrolyses:



binds to cellular DNA

Platinum based drugs have annual sales in excess of \$2B.

Hydrates

$[Co(H_2O)_6](ClO_4)_2$ $Co(ClO_4)_2 \cdot 6\ H_2O$

$[CuSO_4] \cdot 5\ H_2O$ $[Cu(H_2O)_4][SO_4 \cdot H_2O]$

$BaCl_2 \cdot 2\ H_2O$ *lattice water*

$KAl(SO_4)_2 \cdot 12\ H_2O$ *In alums, some water is coordinated to an ion and some is lattice water*

Stabilization of Oxidation States

$$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq) \qquad E° = +1.82\ V$$

Co^{3+} is a strong oxidizing agent and oxidizes water to O_2

$$4\,Co^{3+}(aq) + 2\,H_2O \longrightarrow 4\,Co^{2+}(aq) + 4\,H^+(aq) + O_2(g) \qquad E°_{cell} = +0.59\ V \quad (24.12)$$

strong electron pair donors stabilize high oxidation states

$$Co^{3+}(aq) + 6\,NH_3(aq) \rightleftharpoons [Co(NH_3)_6]^{3+}(aq) \qquad \beta_6 = K_f = 4.5\times10^{33}$$

$$[Co(NH_3)_6]^{3+}(aq) + e^- \longrightarrow [Co(NH_3)_6]^{2+} \qquad E° = +0.10\ V$$

Photography: Fixing a Photographic Film

exposure $Ag^{+}Br^{-}\text{ (in the lattice)} \xrightarrow{h\nu} Ag^{0}Br^{0}$ defects in the crystal lattice

fixing $$AgBr(s) + 2\,S_2O_3^{\,2-} \longrightarrow [Ag(S_2O_3)_2]^{3-}(aq) + Br^{-}(aq) \qquad (24.13)$$

Black metallic Ag remains on the film, while the unexposed AgBr is removed.

A negative image is created. Photographic paper is then exposed to light shining through the negative, and the same process then produces the corresponding positive image.

Qualitative Analysis

(a)

(b)

(c)

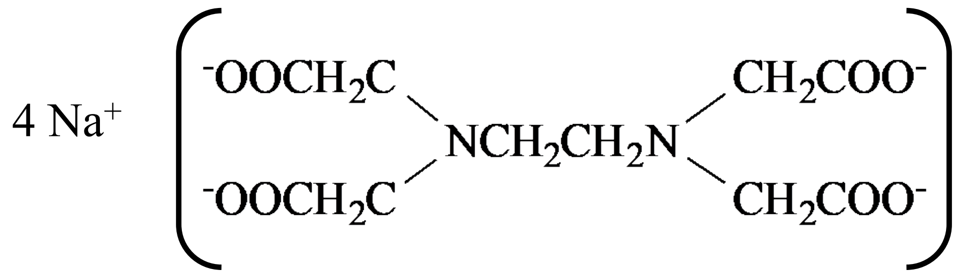
$[Co(SCN)_4]^{2-}$
complex ion

$[Fe(H_2O)_4(SCN)]^{2+}$
complex ion

mixture of
$[FeF_6]$ and $[Co(SCN)_4]^{2-}$
complex ion

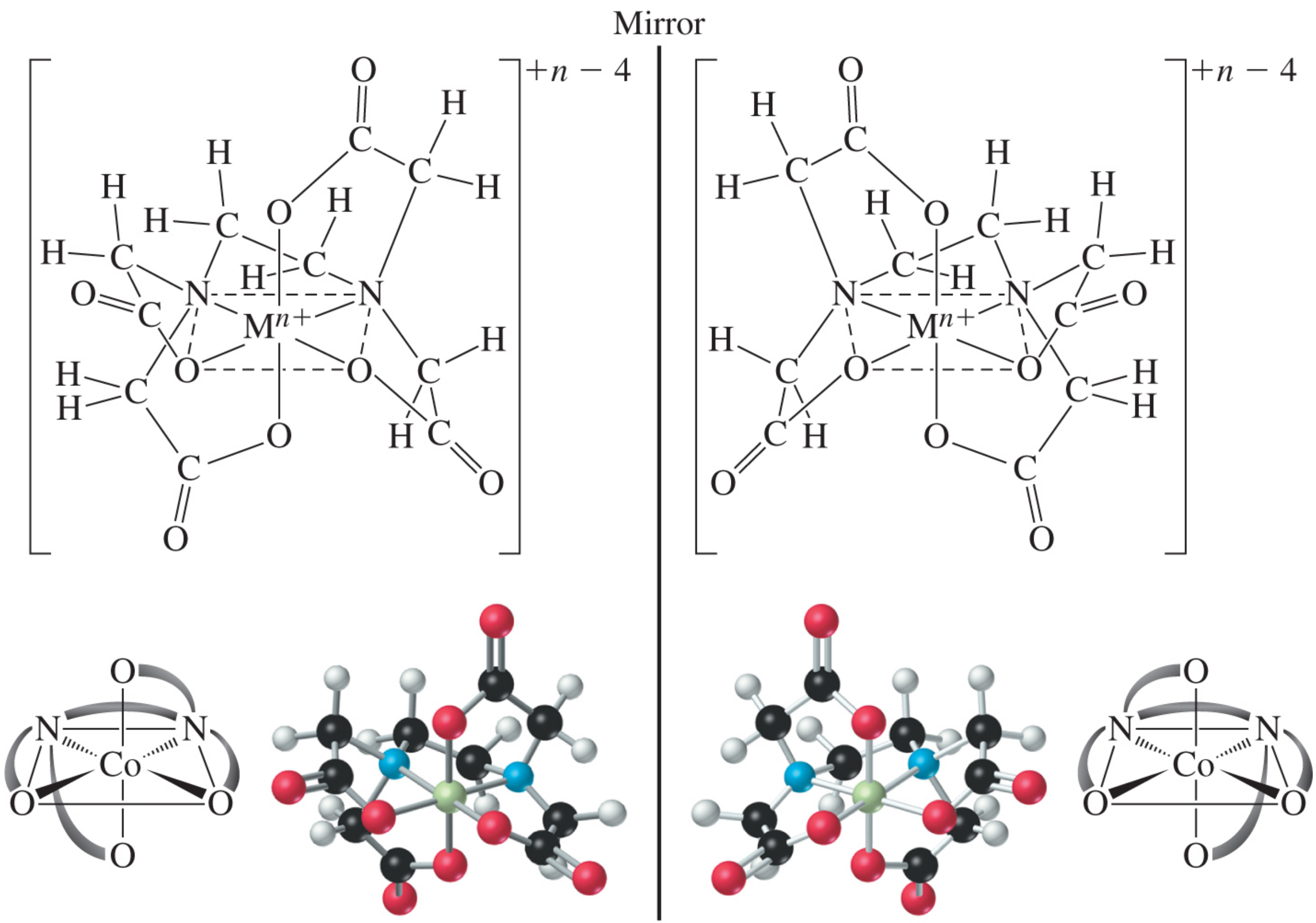
▲ FIGURE 24-22
Qualitative tests for Co^{2+} and Fe^{3+}

Sequestering Metal Ions



sodium salt of *ethylenediaminetetraacetic acid* (Na_4EDTA)

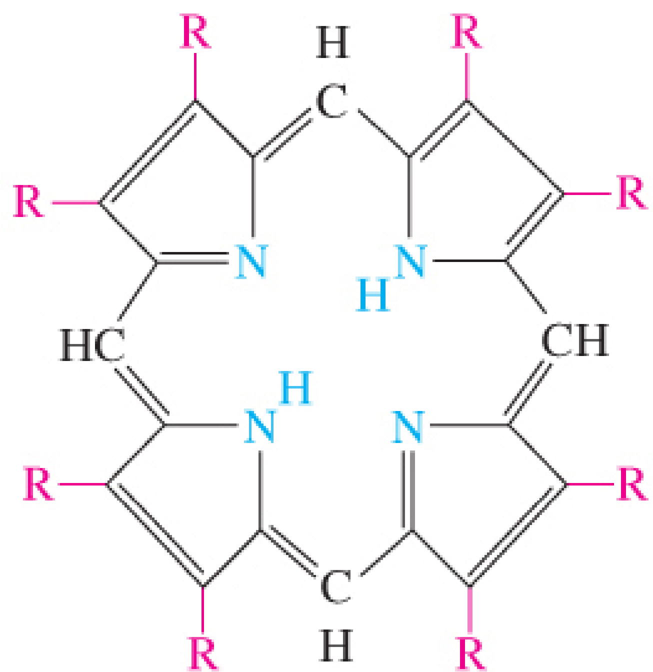
A chelating agent



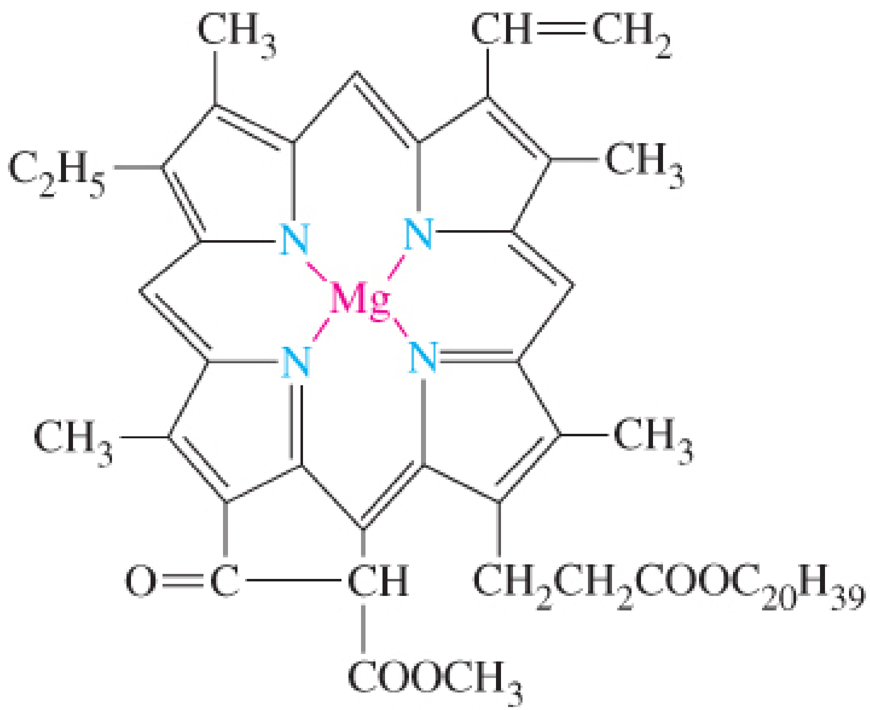
▲ FIGURE 23-23

Structure of a metal-EDTA complex

Biological Applications: Porphyrins



▲ FIGURE 24-24
The porphyrin structure



▲ FIGURE 24-25
Structure of chlorophyll *a*

End of Chapter

