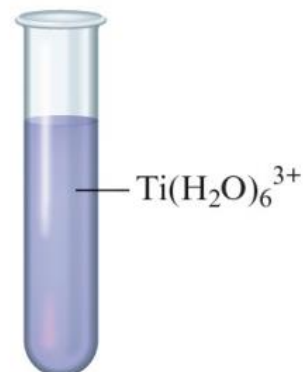
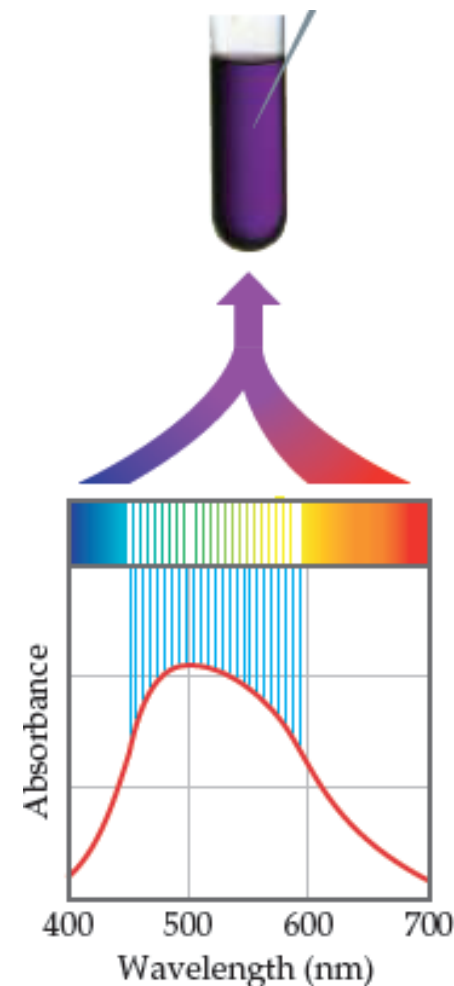


When white shines on a filter that absorbs in the yellow-green region, the emerging light is violet.

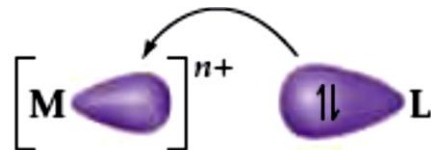


Because the complex ion $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ absorbs yellow-green light, a solution of it is violet.

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

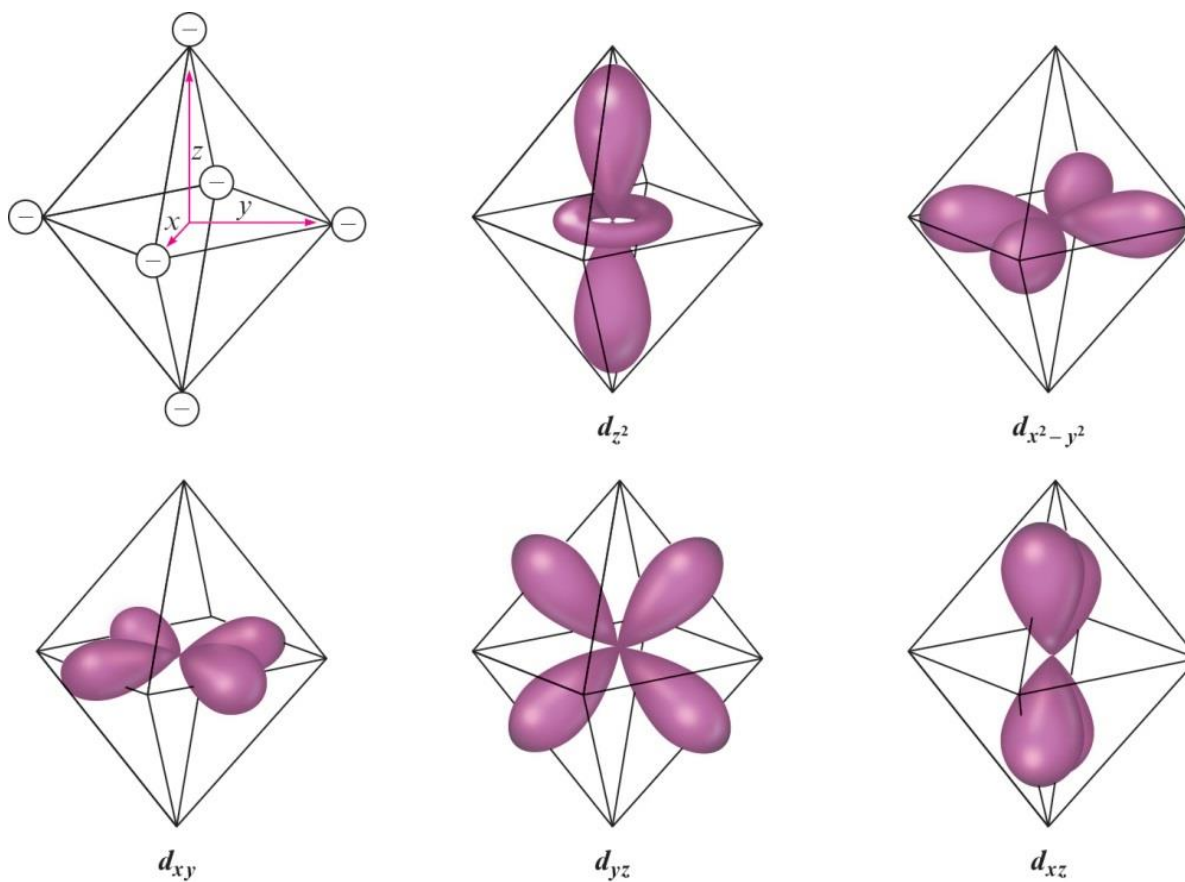


▲ **Figure 23.26** The color of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. A solution containing the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion appears purple because, as its visible absorption spectrum shows, the solution does not absorb light from the violet and red ends of the spectrum. That unabsorbed light is what reaches our eyes.

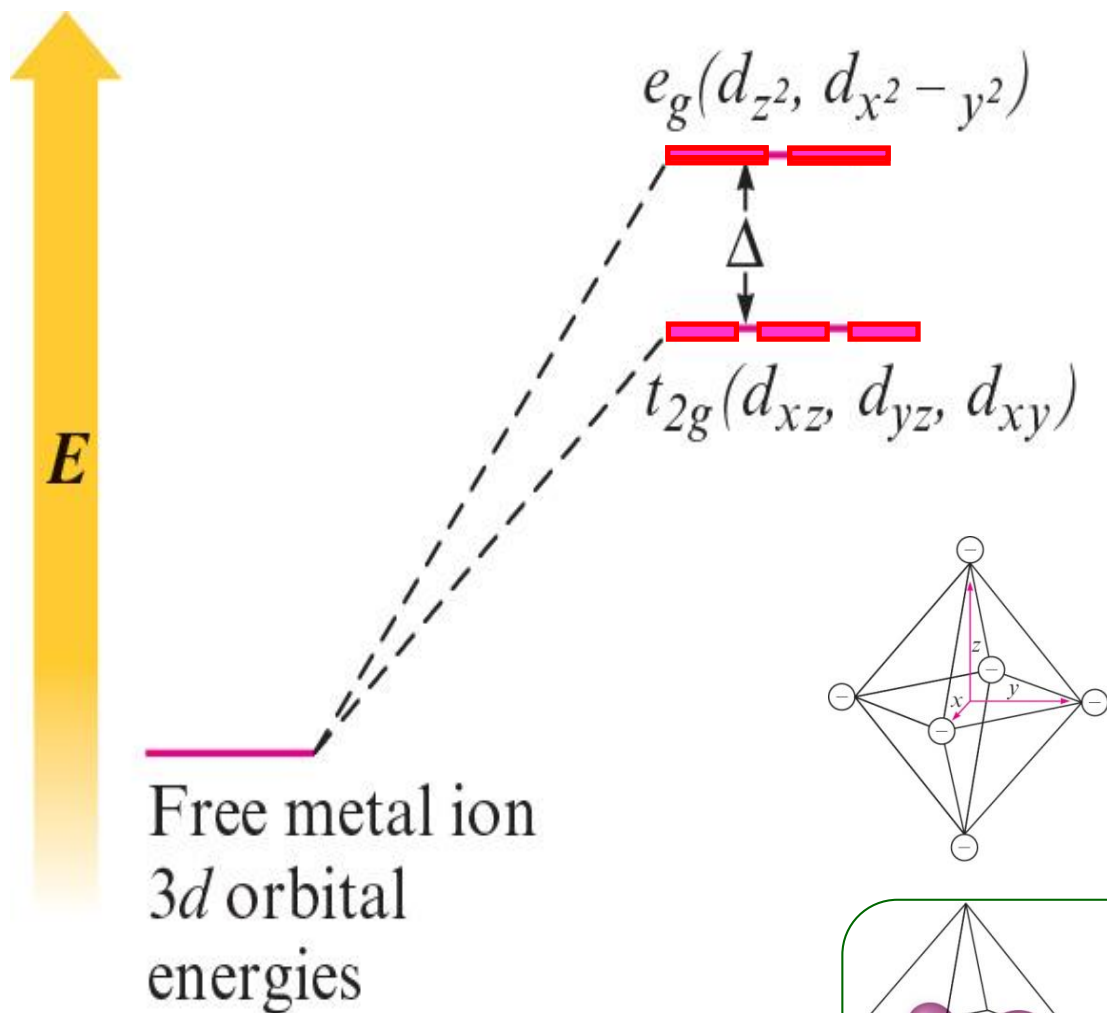


▲ **Figure 23.27** Metal–ligand bond formation. The ligand acts as a Lewis base by donating its nonbonding electron pair to an empty orbital on the metal ion. The bond that results is strongly polar with some covalent character.

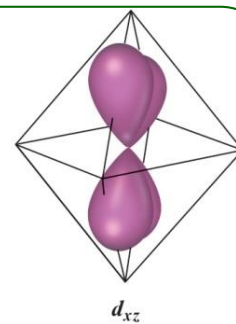
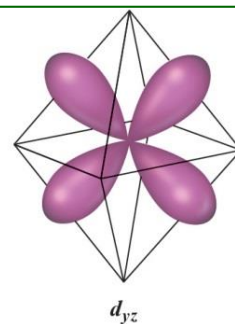
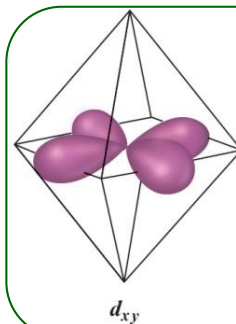
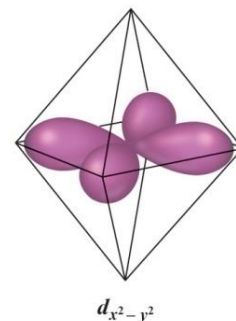
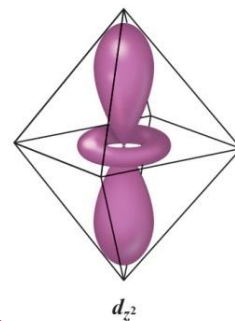
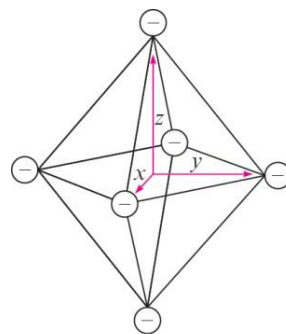
3d Orbitals



Splitting of 3d Orbital Energies (Δ)

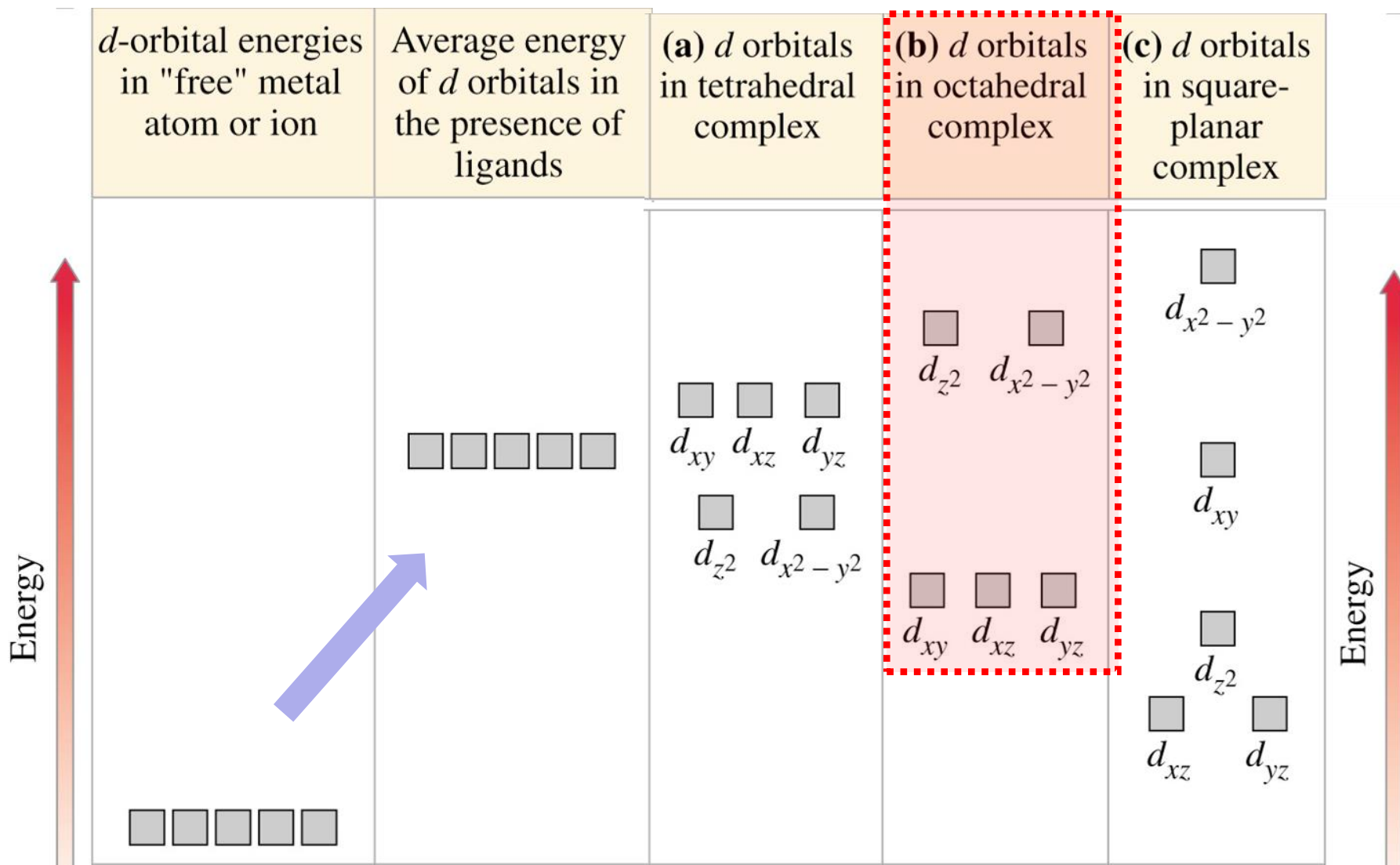


Explains the color and magnetism of complex ions of the first-row transition metal ions



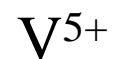
Energies of the 3d orbitals for a metal ion in an octahedral complex.

Crystal field *d*-Level Splitting



21	Scandium	[Ar] 4s ² 3d ¹
22	Titanium	[Ar] 4s ² 3d ²
23	Vanadium	[Ar] 4s ² 3d ³

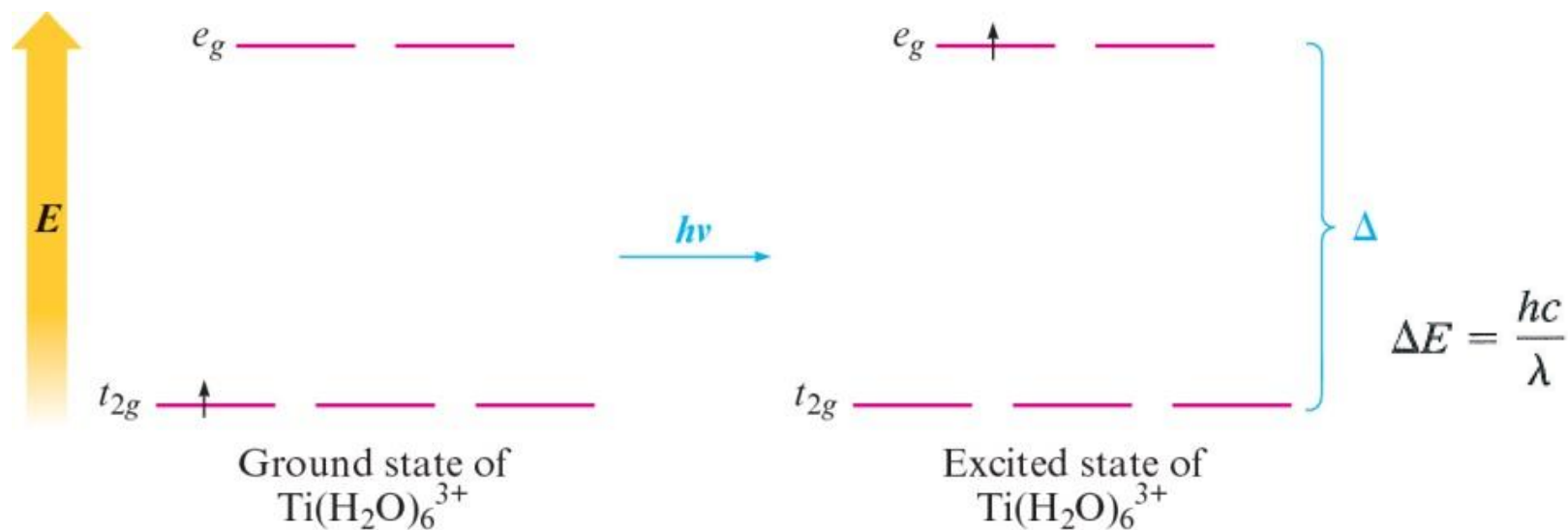
***d*⁰ system**



***d*¹ system**



***d*² system**



Many complex ions are colored because **the energy differences between *d* orbitals** match the energies of components of visible light

Transition Metal Ions Lend Color to Gems

The beautiful pure color of gems, so valued by cultures everywhere, arises from trace transition metal ion impurities in minerals that would otherwise be colorless. For example, the stunning red of a ruby, the most valuable of all gemstones, is caused by Cr^{3+} ions, which replace about 1% of the Al^{3+} ions in the mineral corundum, which is a form of aluminum oxide (Al_2O_3) that is nearly as hard as diamond. In the corundum structure the Cr^{3+} ions are surrounded by six oxide ions at the vertices of an octahedron. This leads to the characteristic octahedral splitting of chromium's 3d orbitals, such that the Cr^{3+} ions absorb strongly in the blue-violet and yellow-green regions of the visible spectrum but transmit red light to give the characteristic ruby color. (On the other hand, if some of the Al^{3+} ions in the corundum are replaced by a mixture of Fe^{2+} , Fe^{3+} , and Ti^{4+} ions, the gem is a sapphire with its brilliant blue color; or if some of the Al^{3+} ions are replaced by Fe^{2+} ions, the stone is a yellow topaz.)

Emeralds are derived from the mineral beryl, a beryllium aluminum silicate (empirical formula $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$). When some of the Al^{3+} ions in beryl are replaced by Cr^{3+} ions, the characteristic green color of emerald

results. In this environment the splitting of the Cr^{3+} 3d orbitals causes it to strongly absorb yellow and blue-violet light and to transmit green light.

A gem closely related to ruby and emerald is alexandrite, named after Alexander II of Russia. This gem is based on the mineral chrysoberyl, a beryllium aluminate with the empirical formula $\text{BeO} \cdot \text{Al}_2\text{O}_3$ in which approximately 1% of the Al^{3+} ions are replaced by Cr^{3+} ions. In the chrysoberyl environment Cr^{3+} absorbs strongly in the yellow region of the spectrum. Alexandrite has the interesting property of changing colors depending on the light source. When the first alexandrite stone was discovered deep in a mine in the Russian Ural Mountains in 1831, it appeared to be a deep red color in the firelight of the miners' lamps. However, when the stone was brought to the surface, its color was blue. This seemingly magical color change occurs because the firelight of a miner's helmet is rich in the yellow and red wavelengths of the visible spectrum but does not contain much blue. Absorption of the yellow by the stone produces a reddish color. However, daylight has much more intensity in the blue region than firelight. Thus the extra blue in the light transmitted by

the stone gives it bluish color in daylight.

Once the structure of a natural gem is known, it is usually not very difficult to make the gem artificially. For example, rubies and sapphires are made on a large scale by fusing $\text{Al}(\text{OH})_3$ with the appropriate transition metal salts at approximately 1200°C to make the "doped" corundum. With these techniques gems of astonishing size can be manufactured: Rubies as large as 10 lb and sapphires up to 100 lb have been synthesized. Smaller synthetic stones produced for jewelry are virtually identical to the corresponding natural stones, and it takes great skill for a gemologist to tell the difference.



Alexandrite, a gem closely related to ruby and emerald.

Chapter 23 Transition Metals and Coordination Chemistry

The importance of transition metals such as iron and copper, is not limited to biology and medicine. Transition metals and their alloys are used as structural materials to make coins and jewelry, and as electronic conductors in wires and electronic devices. The presence of partially filled *d*-orbitals allows transition metal compounds to act as catalysts, magnets, and pigments. In this chapter, we take a closer look at this fascinating group of elements.

TABLE 23.2 Properties of the Period 4 Transition Metals

Group	3	4	5	6	7	8	9	10	11	12
Element:	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Ground-state electron configuration	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$
First ionization energy (kJ/mol)	631	658	650	653	717	759	758	737	745	906
Metallic radius (pm)	164	147	135	129	137	126	125	125	128	137
Density (g/cm ³)	3.0	4.5	6.1	7.9	7.2	7.9	8.7	8.9	8.9	7.1
Melting point (°C)	1541	1660	1917	1857	1244	1537	1494	1455	1084	420
Crystal structure*	hcp	hcp	bcc	bcc	**	bcc	hcp	fcc	fcc	hcp

*Abbreviations for crystal structures are **hcp** = hexagonal close packed, **fcc** = face-centered cubic, **bcc** = body-centered cubic. (Section 12.3)

Structure types of Metals

Structure types of Metals																		
H																		He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac																



Simple cubic



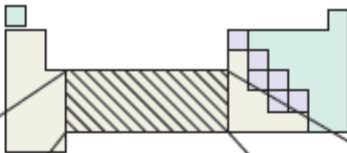
Cubic close packing
(Face centered cubic)



Body centered cubic



Hexagonal close packing



3	4	5	6	7	8	9	10	11	12
21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg

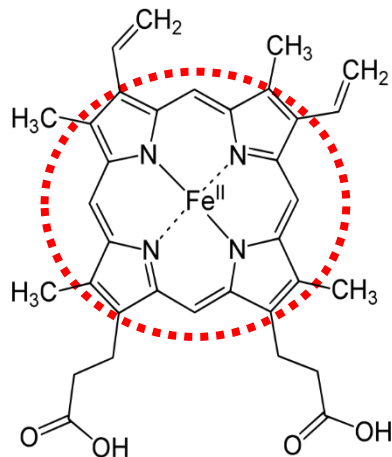
▲ **Figure 23.2** The position of the transition metals in the periodic table. They are groups 3-12 in periods 4, 5, and 6. The short-lived, radioactive transition metals from period 7 are not shown.

Humans, like all vertebrates, have red blood. The red color is due to an iron-containing protein called hemoglobin found in red blood cells. Hemoglobin is responsible for binding oxygen in the lungs and transporting it to cells throughout the body.

Myoglobin: Oxygen storage molecule

Biological Necessity of Metal Ion Complexes

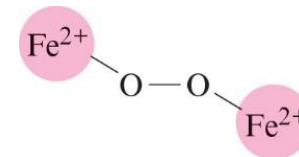
the Heme complex



Containing ferrous where the Fe²⁺ ion is coordinated to four nitrogen atoms

It consists of a heme complex and a protein chain (one N from the protein coordinates to Fe²⁺ ion).

The sixth coordination position is water which is available for an oxygen molecule



When gaseous O₂ is bubbled in an aqueous solution containing heme (血紅素), Fe²⁺ is oxidized to Fe³⁺ (an O₂ bridge between Fe²⁺ ions)

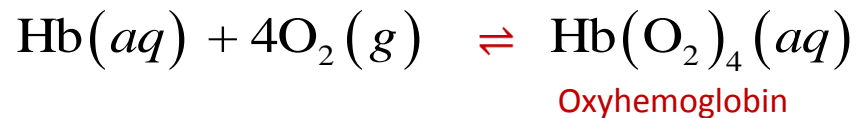
Role of Iron in the Transportation of Oxygen in Mammals

Hemoglobin (Hb): Molecule that contains four myoglobin-like units (...helps in the transportation of oxygen in the blood)

Each hemoglobin can bind four oxygen molecules to form a bright red diamagnetic complex.

When the oxygen molecule is released, water molecules occupy the sixth coordination position around each Fe^{2+}

Reaction between hemoglobin and oxygen



Effect of High Altitudes on Humans

Oxygen content in high altitudes is low

The above equilibrium will shift to the left according to Le Châtelier's principle.

Lower levels of oxyhemoglobin cause fatigue, dizziness, and high-altitude sickness

The human body is capable of adapting to lower levels of oxygen by making more haemoglobin

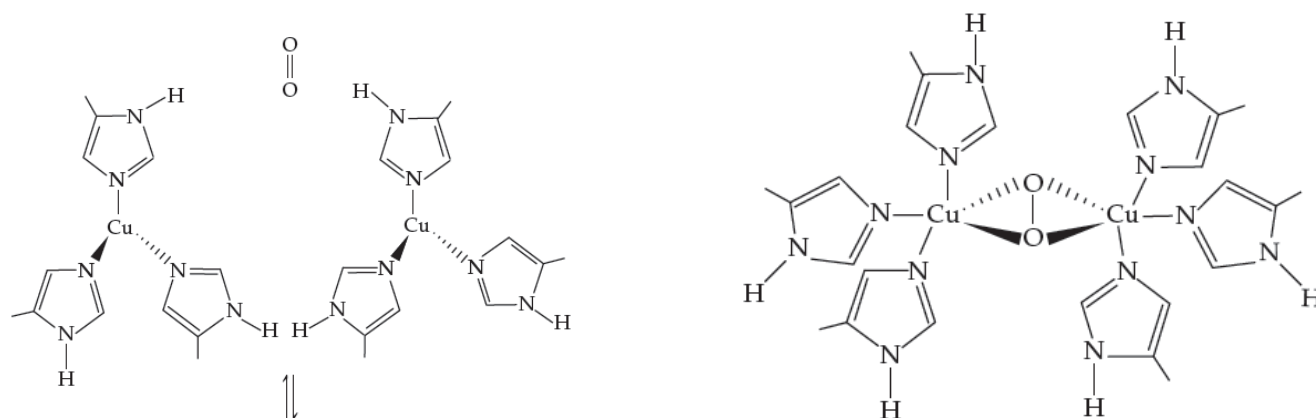
Causes the equilibrium to shift back to the right.

High-altitude acclimatization

Effect of high altitude can be felt for a few weeks, but it disappears

as hemoglobin levels in the body increase

However, not all animals have red blood. Some marine animals, including octopuses, squids, and lobsters, have blue blood because they rely on a copper-containing protein called hemocyanine for transporting oxygen. In the deoxygenated state, hemocyanine contains two Cu^+ ions separated from each other by over 400 pm, a distance too long to form a bond. When an oxygen molecule encounters this site in the protein, an electron transfer reaction takes place in which the O_2 molecule is reduced to the peroxide ion, O_2^{2-} , while both copper ions are oxidized to Cu^{2+} , as shown in **Figure 23.1**. The presence of Cu^{2+} ions in oxygenated hemocyanine is responsible for the blue color of the blood.



▲ **Figure 23.1** Hemocyanine binds oxygen. The Cu^+ ions are each bound by three nitrogen atoms from the hemocyanine protein in the deoxygenated state (left). As the O_2 molecule binds between the Cu^+ ions, it is reduced to O_2^{2-} while the Cu^+ ions are oxidized to Cu^{2+} ions.

Among the blue bloods of the animal kingdom, the blood of the horseshoe crab is the most valuable. That's because the primitive immune system of the horseshoe crab contains a substance called limulus amoebocyte lysate (LAL), which protects the crabs from infection by binding to potentially harmful viruses and bacterial endotoxins. It was discovered in the early 1960s that LAL could be used to detect trace amounts of toxic substances in drugs and medical devices. The U.S. Food and Drug Administration now requires that all drugs intended for

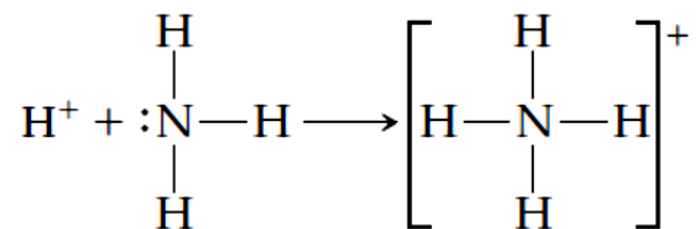
To obtain sufficient quantities of LAL for the pharmaceutical industry, people harvest horseshoe crabs, attach them to machines that drain off roughly 30% of their blood, and then return them to the ocean. The LAL that is extracted from the blood can sell for up to \$15,000 per quart. Most animals survive the ordeal, the mortality rate is estimated to be between 5 and 30%, although questions have been raised regarding the effects of this invasive process on the overall health of the wild population of horseshoe crabs.

The horseshoe crab and public health

If you've ever had a flu shot, know someone with a pace maker or joint replacement, or have given your pet a rabies vaccination, you owe a debt of gratitude to the horseshoe crab. Vaccines, injectable drugs, intravenous solutions, and implantable medical devices, both for humans and animals, are quality checked for safety using a test that comes from the blood of horseshoe crabs.

16.11 | Lewis Acids and Bases

For a substance to be a proton acceptor (a Brønsted–Lowry base), it must have an unshared pair of electrons for binding the proton, as, for example, in NH_3 . Using Lewis structures, we can write the reaction between H^+ and NH_3 as



G. N. Lewis was the first to notice this aspect of acid–base reactions. He proposed a more general definition of acids and bases that emphasizes the shared electron pair:

- A **Lewis acid** is an electron-pair acceptor.
- A **Lewis base** is an electron-pair donor.

many simple cations can function as Lewis acids. For example, Fe^{3+} interacts strongly with cyanide ions to form the ferricyanide ion:



The Fe^{3+} ion has vacant orbitals that accept the electron pairs donated by the cyanide ions. (We will learn more in Chapter 23 about just which orbitals are used by the Fe^{3+} ion.) The metal ion is highly charged, too, which contributes to the interaction with CN^- ions.

The Metal–Ligand Bond

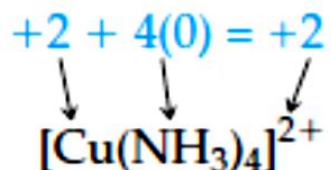
The reaction between a metal and a ligand is a reaction between a Lewis acid (the metal) and a Lewis base (the ligand). The new complex has distinct physical and chemical properties (e.g., color, reduction potential).



Figure 23.9 shows the color change that occurs when aqueous solutions of NCS^- (colorless) and Fe^{3+} (yellow) are mixed, forming $3\text{Fe}(\text{H}_2\text{O})_5\text{NCS}_4^{2+}$.

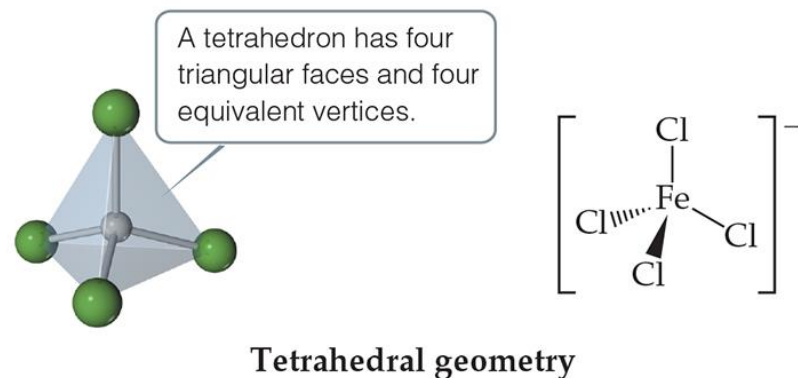
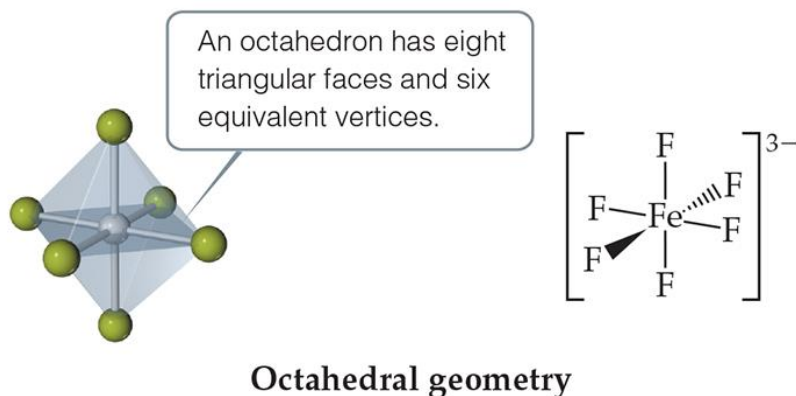
Charges, Coordination Numbers, and Geometries

The charge of a complex is the sum of the charges on the metal and on the ligands. In $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ we can deduce the charge on the complex ion because we know that the charge of the sulfate ion is $2-$. Because the compound is electrically neutral, the complex ion must have a $2+$ charge, $[\text{Cu}(\text{NH}_3)_4]^{2+}$. We can then use the charge of the complex ion to deduce the oxidation number of copper. Because the NH_3 ligands are uncharged molecules, the oxidation number of copper must be $+2$:



The **coordination number** of a metal depends upon the size of the metal and the size of the ligands.

The **coordination number** of a metal depends upon the size of the metal and the size of the ligands.



Iron(III) can bind to 6 fluorides but only 4 chlorides, **why?**

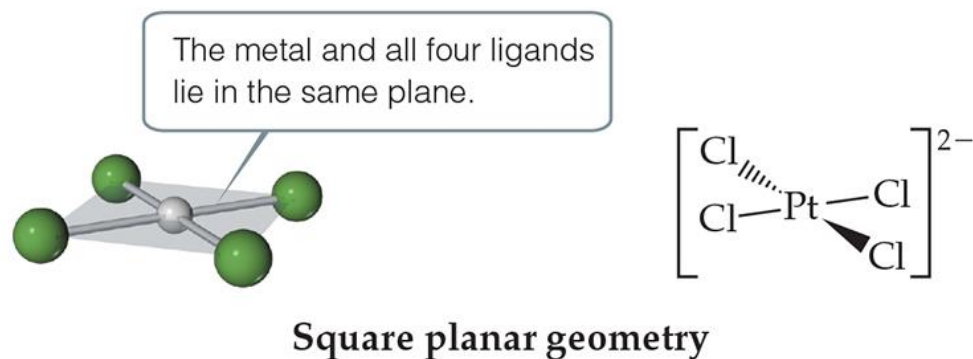
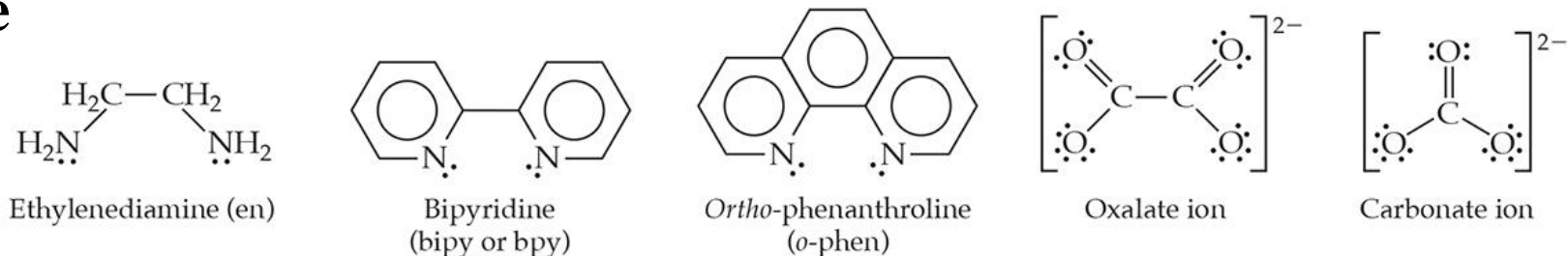


TABLE 23.4 Some Common Ligands

Monodentate

Ligand Type	Examples					
Monodentate	$\text{H}_2\ddot{\text{O}}:$ Water	$:\ddot{\text{F}}:^-$ Fluoride ion	$[:\text{C}\equiv\text{N}:]^-$ Cyanide ion	$[:\ddot{\text{O}}-\text{H}]^-$ Hydroxide ion		
	$:\text{NH}_3$ Ammonia	$:\ddot{\text{Cl}}:^-$ Chloride ion	$[\ddot{\text{S}}=\text{C}=\ddot{\text{N}}:]^-$ Thiocyanate ion <div style="text-align: center;"> \swarrow or \searrow </div>	$[\ddot{\text{O}}-\text{N}=\ddot{\text{O}}:]^-$ Nitrite ion <div style="text-align: center;"> \swarrow or \searrow </div>		

bidentate



Polydentate

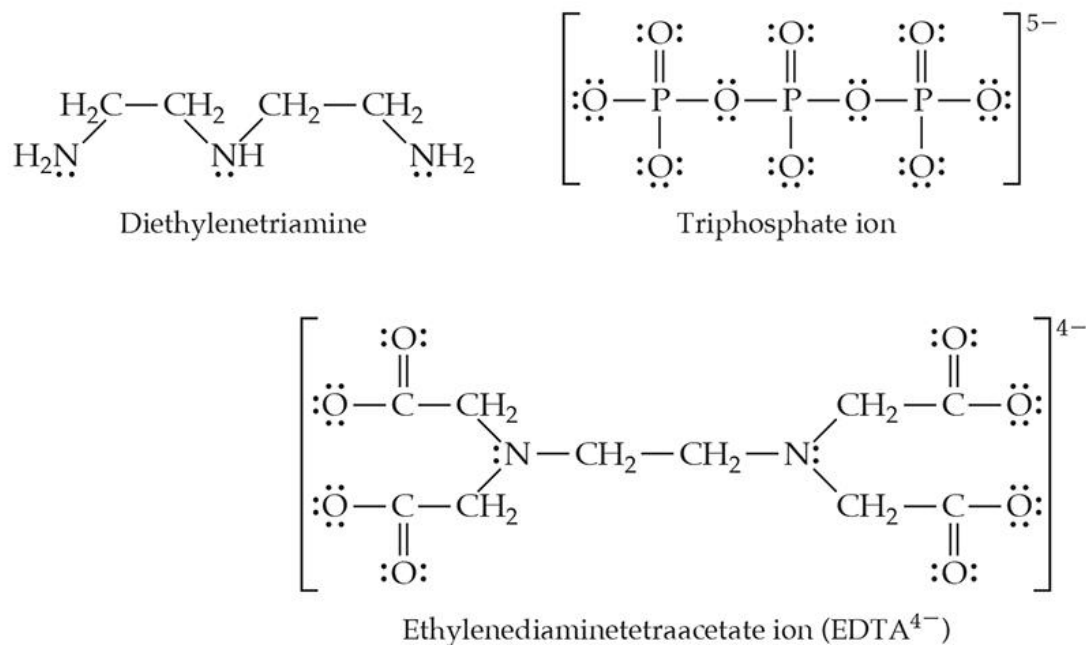
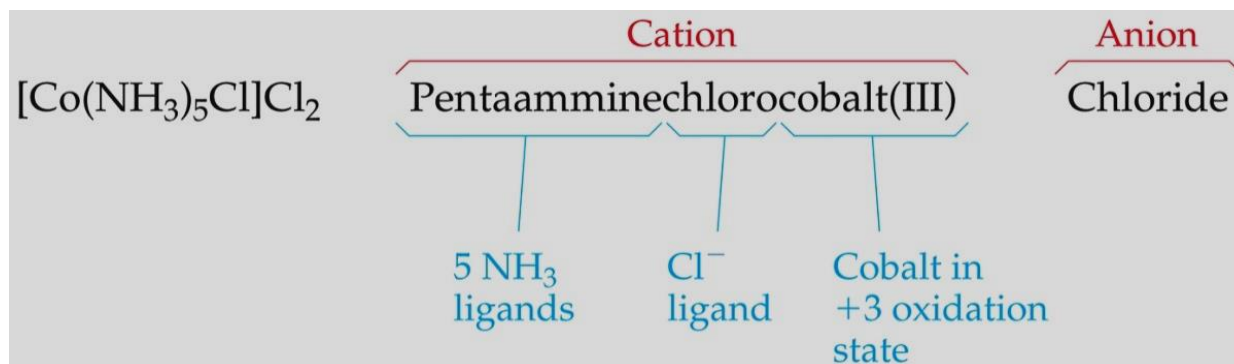


TABLE 23.5 Some Common Ligands and Their Names

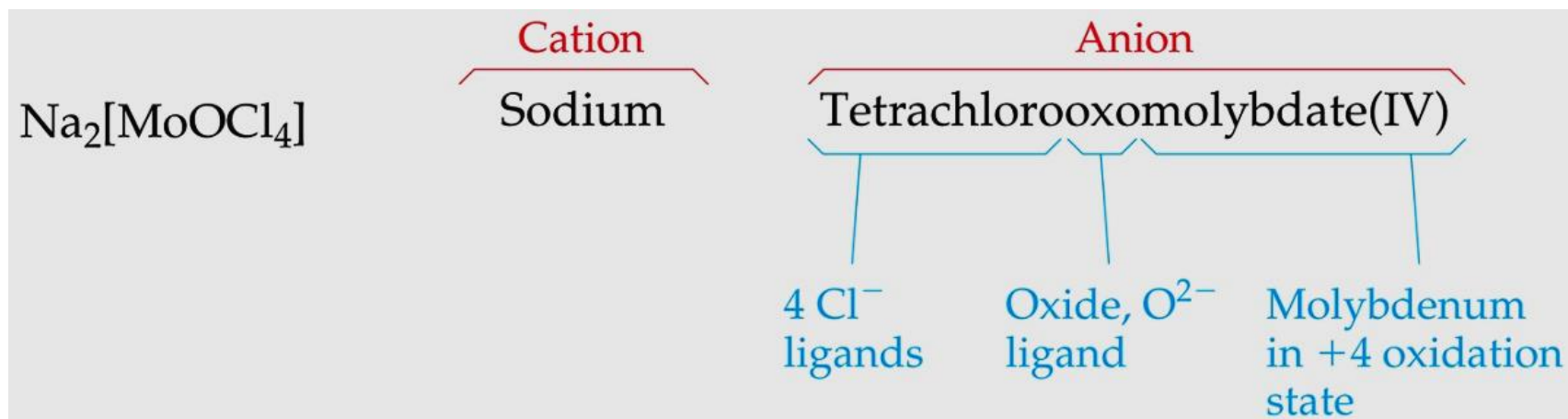
Ligand	Name in Complexes	Ligand	Name in Complexes
Azide, N_3^-	Azido	Oxalate, $\text{C}_2\text{O}_4^{2-}$	Oxalato
Bromide, Br^-	Bromo	Oxide, O^{2-}	Oxo
Chloride, Cl^-	Chloro	Ammonia, NH_3	Ammine
Cyanide, CN^-	Cyano	Carbon monoxide, CO	Carbonyl
Fluoride, F^-	Fluoro	Ethylenediamine, en	Ethylenediamine
Hydroxide, OH^-	Hydroxo	Pyridine, $\text{C}_5\text{H}_5\text{N}$	Pyridine
Carbonate, CO_3^{2-}	Carbonato	Water, H_2O	Aqua

Nomenclature Rules for Coordination Chemistry

1. In naming complexes that are salts, the name of the cation is given before the name of the anion.
2. In naming complex ions or molecules, the ligands are named before the metal. Ligands are listed in alphabetical order, regardless of their charges.



3. The names of anionic ligands end in the letter *o*, but electrically neutral ligands ordinarily bear the name of the molecules (exceptions: ammonia, water, CO).



4. Greek prefixes (*di-*, *tri-*, *tetra-*, etc.) are used to indicate the number of each kind of ligand when more than one is present. If the ligand contains a Greek prefix or is polydentate, the prefixes *bis-*, *tris-*, *tetrakis-*, and so on are used, and the ligand name is placed in parentheses.
5. If the complex is an anion, its name ends in *-ate*.
6. The oxidation number of the metal is given in parentheses in Roman numerals following the name of the metal.

Examples

- $[\text{Ni}(\text{NH}_3)_6]\text{Br}_2$ = hexaamminenickel(II) bromide
- $\text{Na}_2[\text{MoOCl}_4]$ = sodium tetrachlorooxomolybdate(IV)
- $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{CN})]\text{Cl}_2$ = aquacyanobis(ethylenediamine)cobalt(III) chloride

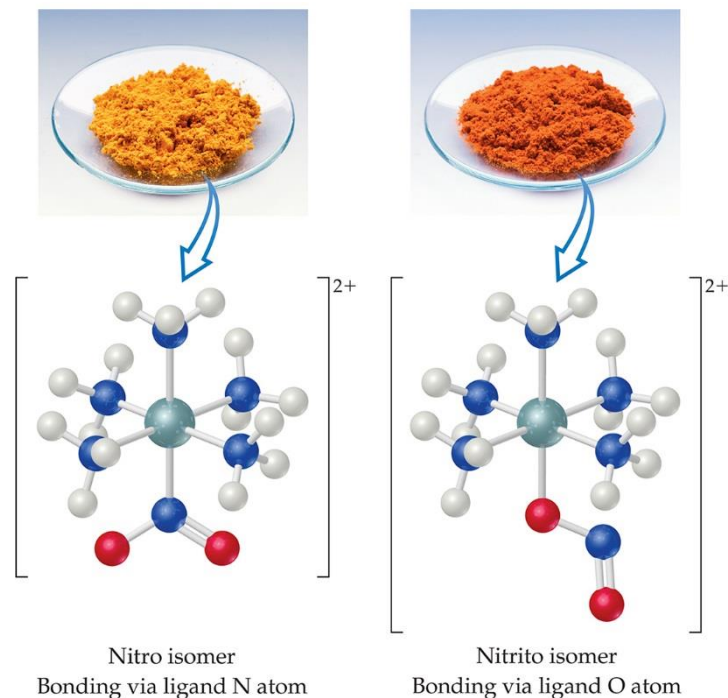
Isomers

--- have the **same** molecular **formula** but a **different arrangement of atoms**.

There are two main subgroupings: **structural isomers** (same molecular formula but different connections of atoms) and **stereoisomers** (same connections of atoms, but different three-dimensional orientations).

Linger isomers

---isomers the ligand is bound to the metal by a different atom. For example, nitrite can bind via the N or via an O.



Coordination sphere isomers differ

in what ligands are bound to the metal and which fall outside the coordination sphere.

For example, $\text{CrCl}_3(\text{H}_2\text{O})_6$ exists as $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$, or $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$.

TABLE 23.3 Properties of Some Ammonia Complexes of Cobalt(III)

Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$\text{CoCl}_3 \cdot 6 \text{NH}_3$	Orange	4	3	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
$\text{CoCl}_3 \cdot 5 \text{NH}_3$	Purple	3	2	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
$\text{CoCl}_3 \cdot 4 \text{NH}_3$	Green	2	1	<i>trans</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
$\text{CoCl}_3 \cdot 4 \text{NH}_3$	Violet	2	1	<i>cis</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

Sample Exercise 23.3

Naming Coordination Compounds

Name the compounds **(a)** $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$, **(b)** $\text{K}_4[\text{Ni}(\text{CN})_4]$.

► Practice Exercise 1

What is the name of the compound $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$?

- (a)** Rhodium(III) tetraamminedichloro chloride
(b) Tetraammoniadichlororhodium(III) chloride **(c)** Tetraamminedichlororhodium(III) chloride **(d)** Tetraamminetrichlororhodium(III) **(e)** Tetraamminedichlororhodium(II) chloride

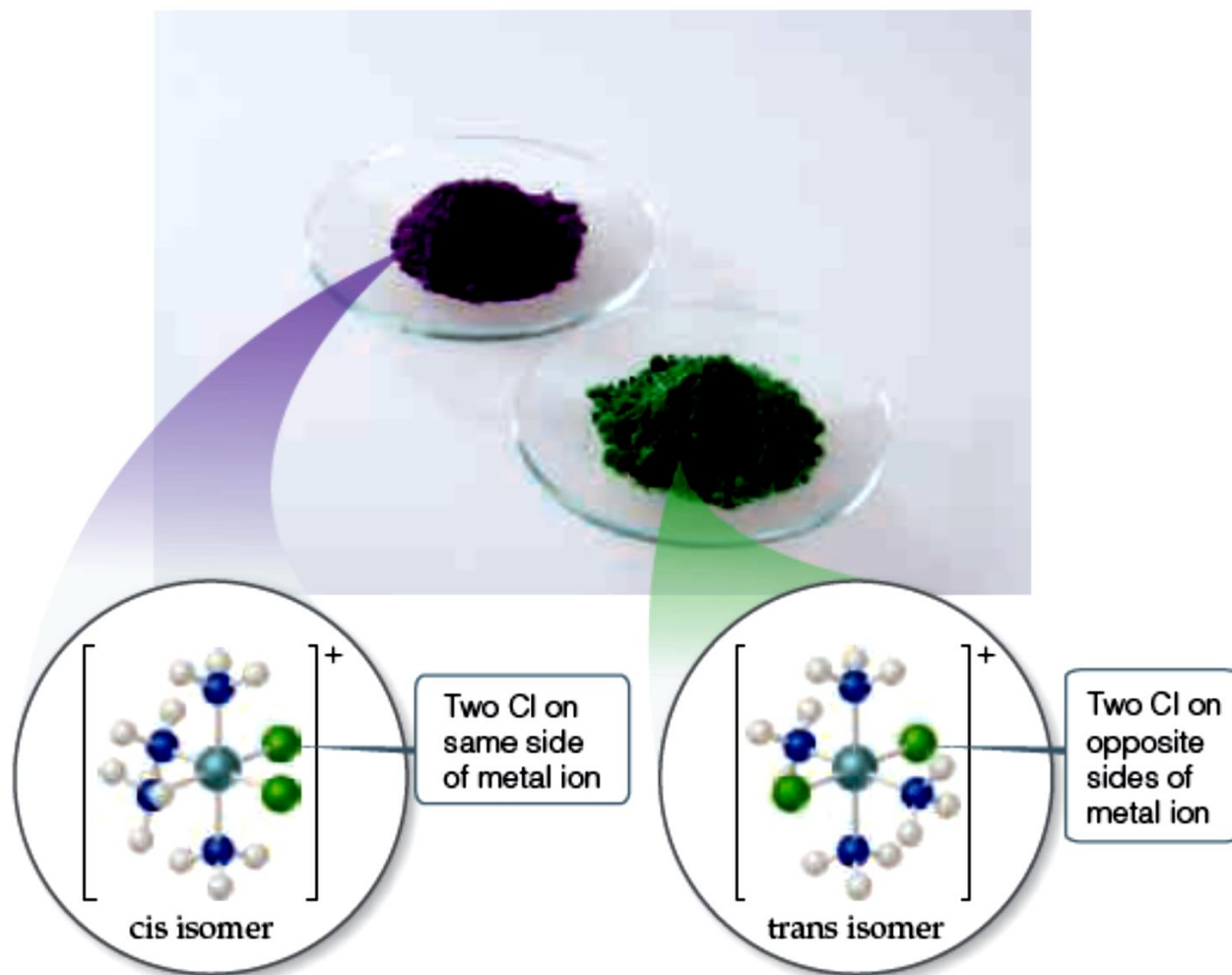
► Practice Exercise 2

Name the compounds **(a)** $[\text{Mo}(\text{NH}_3)_3\text{Br}_3]\text{NO}_3$, **(b)** $(\text{NH}_4)_2[\text{CuBr}_4]$. **(c)** Write the formula for sodium diaquabis(oxalato)ruthenate(III).



Go Figure

Is there another way to arrange the chloride ions in the $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ ion besides the two shown in this figure?



▲ **Figure 23.8** Isomers of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$. The cis isomer is violet, and the trans isomer is green.