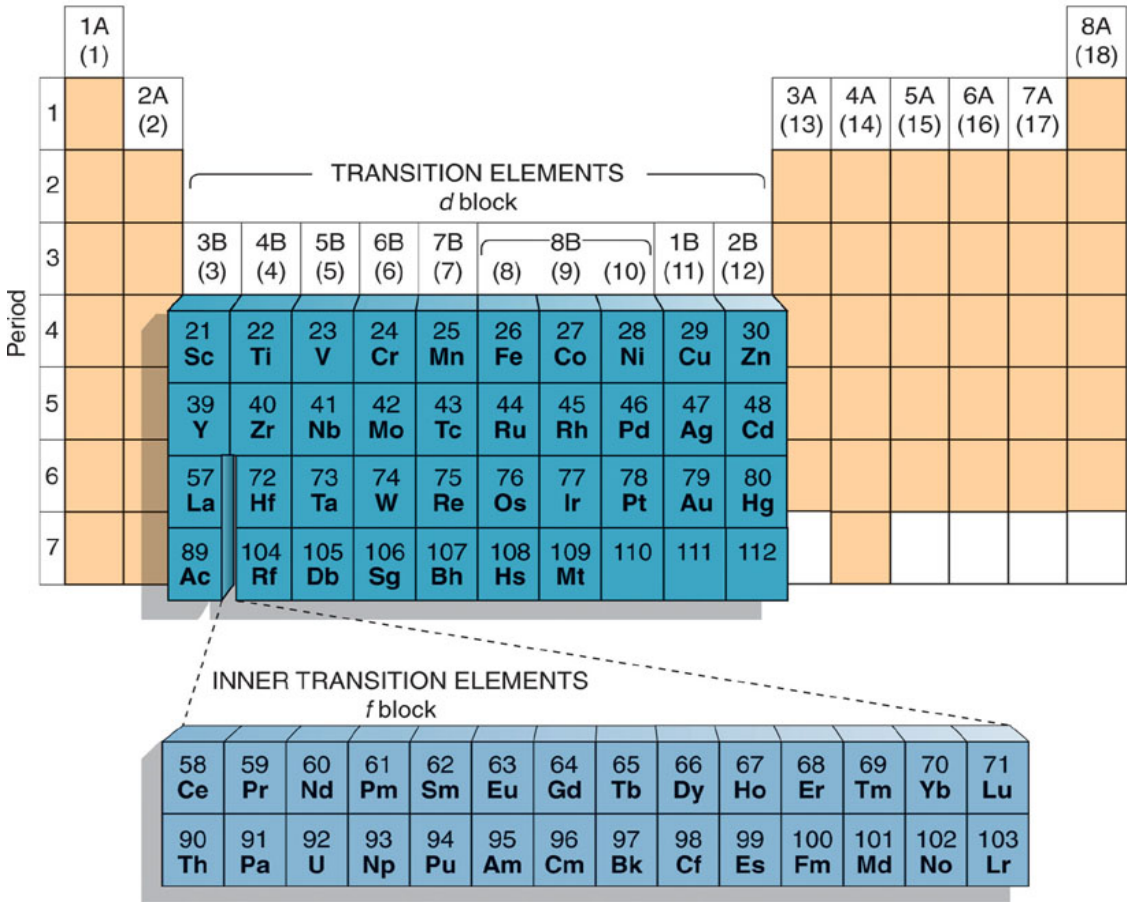
Chapter 16 – The Elements: The *d*-Block

- The *d*-Block Elements and Their Compounds
- Select Elements: A Survey
- Coordination Compounds
- The Electronic Structure of Complexes

The d-Block Elements and Their Compounds

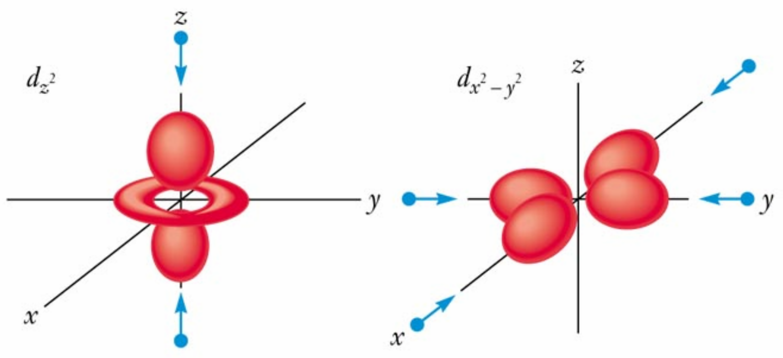
Location on Periodic Table



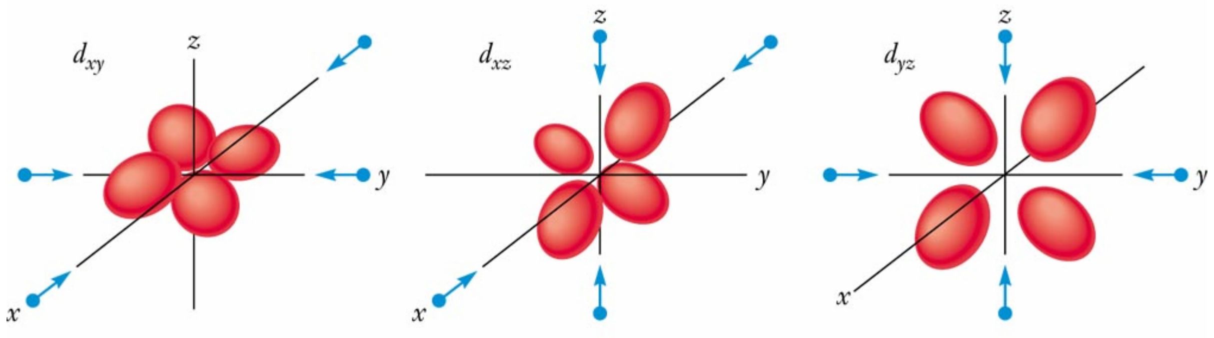
Transition metals, are located in groups 3 through 11. They are called transition metals because they transition between the highly reactive *s* block metals and the much less reactive metals of group 12 and the *p* block.

The d-Block Elements and Their Compounds

Shape of *d* Orbitals



Large repulsions

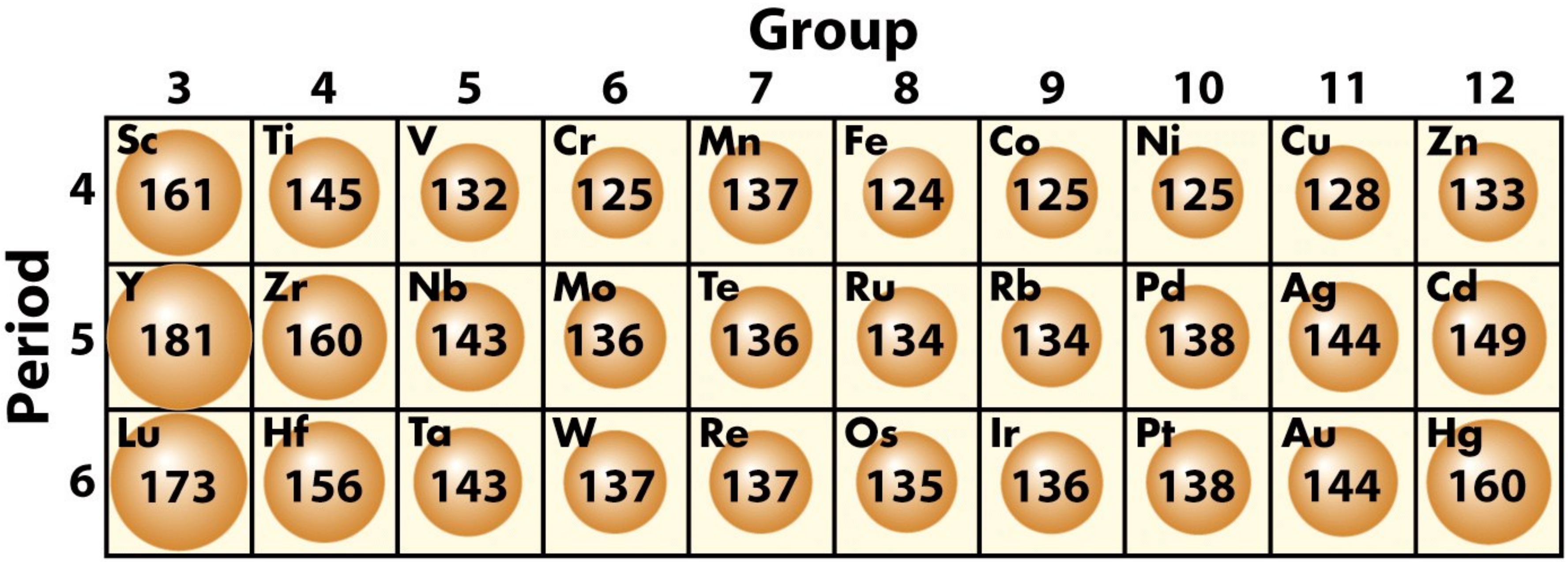


Smaller repulsions

The shape of the *d* orbitals affect the properties of transition metals. The *d* orbital lobes are far apart and so only weakly repel each other. The *d* orbitals have low electron density near the nucleus therefore are not very effective at shielding.

The *d*-Block Elements and Their Compounds

Trends in Atomic Radii

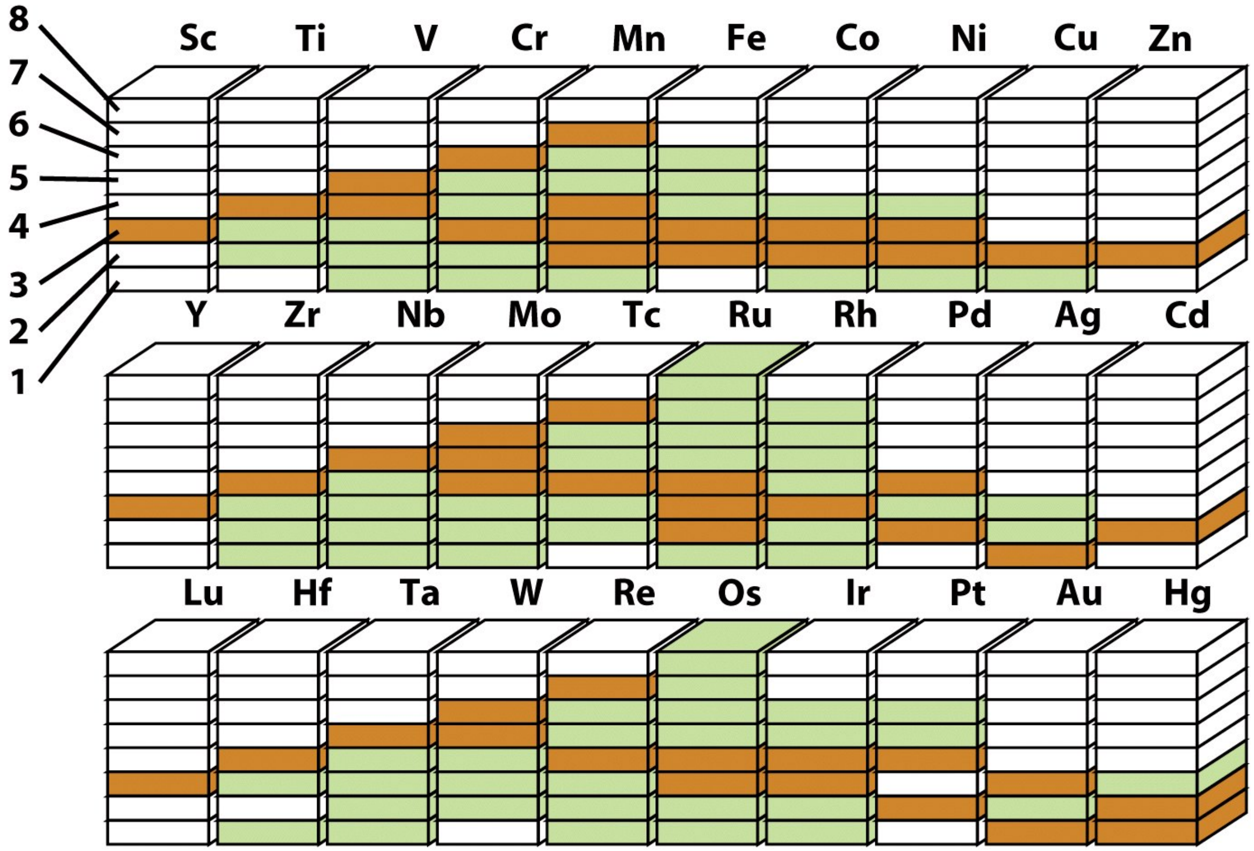


Period \ Group	3	4	5	6	7	8	9	10	11	12
4	Sc 161	Ti 145	V 132	Cr 125	Mn 137	Fe 124	Co 125	Ni 125	Cu 128	Zn 133
5	Y 181	Zr 160	Nb 143	Mo 136	Te 136	Ru 134	Rb 134	Pd 138	Ag 144	Cd 149
6	Lu 173	Hf 156	Ta 143	W 137	Re 137	Os 135	Ir 136	Pt 138	Au 144	Hg 160

The shape of the *d* orbitals affect the properties of transition metals. The *d* orbital lobes are far apart and thus only weakly repel each other. The *d* orbitals have low electron density near the nucleus therefore are not very effective at shielding.

The *d*-Block Elements and Their Compounds

Oxidation States



Orange boxes are common oxidation numbers.

Green boxes are other know states.

Most *d*-block metals have more that one oxidation state other than 0. Elements close to the center of the row have the widest rage of oxidation numbers.

Select Elements: A Survey

Scandium Through Nickel

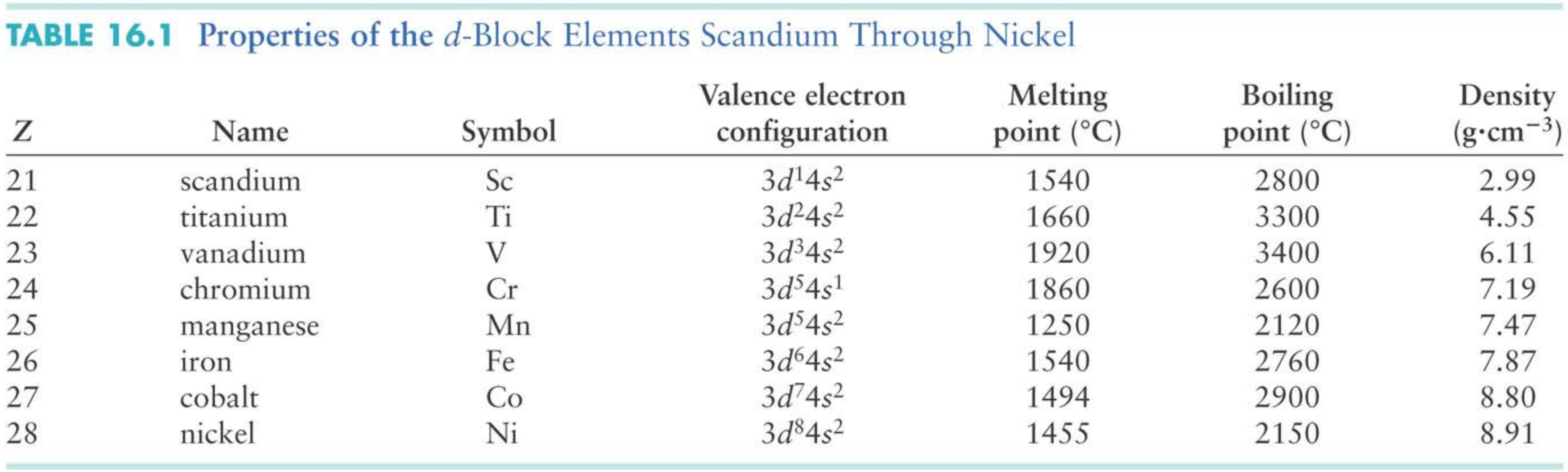


TABLE 16.1 Properties of the *d*-Block Elements Scandium Through Nickel

Z	Name	Symbol	Valence electron configuration	Melting point (°C)	Boiling point (°C)	Density (g·cm^{-3})
21	scandium	Sc	$3d^1 4s^2$	1540	2800	2.99
22	titanium	Ti	$3d^2 4s^2$	1660	3300	4.55
23	vanadium	V	$3d^3 4s^2$	1920	3400	6.11
24	chromium	Cr	$3d^5 4s^1$	1860	2600	7.19
25	manganese	Mn	$3d^5 4s^2$	1250	2120	7.47
26	iron	Fe	$3d^6 4s^2$	1540	2760	7.87
27	cobalt	Co	$3d^7 4s^2$	1494	2900	8.80
28	nickel	Ni	$3d^8 4s^2$	1455	2150	8.91

As you go across the first period of *d*-metals from scandium through nickel you can see there are similarities in the melting and boiling points. In addition, their densities increase as you go across the period.

Select Elements: A Survey

Scandium Through Nickel

	Scandium (Sc)	**Titanium (Ti)**	**Vanadium (V)**	**Chromium (Cr)**
Facts	• Reacts vigorously with water	• Resistant to corrosion (protective oxide skin) • Requires strong reducing agent for extraction from, its ores	• Vanadium compounds come in a wide range of color due to its many oxidation states	• Corrosion resistant
Uses	• Few uses • Not essential to life	• Jet engines •Dental applications	• Makes tough steels for automobile and truck springs • Glazes for ceramics	• Stainless steel • Chrome plating


Scandium, Sc; 3B(3)


Titanium, Ti; 4B(4)


Vanadium, V; 5B(5)


Chromium, Cr; 6B(6)

Select Elements: A Survey

Scandium Through Nickel

	Manganese (Mn)	**Iron (Fe)**	**Cobalt (Co)**	**Nickel (Ni)**
Facts	• Not as corrosion resistant as chromium but more corrosion resistant than iron	• Most widely used d metal • Most abundant element on earth • The second most abundant metal in the earths crust (after aluminum)		• 70% if the western world's nickel comes from ore that was brought close to the earth surface nearly 2 billion year ago by the violent impact of a huge meteor
Uses	• Alloying with steel	• Main component in steel • Essential to life	• Alloying with steal • Used to make permanent magnets found in speakers • Essential to life	• Used to make stainless steal • Nickel is alloyed with copper to make nickel coins


Manganese, Mn; 7B(7)


Iron, Fe; 8B(8)


Cobalt, Co; 8B(9)


Nickel, Ni; 8B(10)

Coordination Compounds

Common Ligands

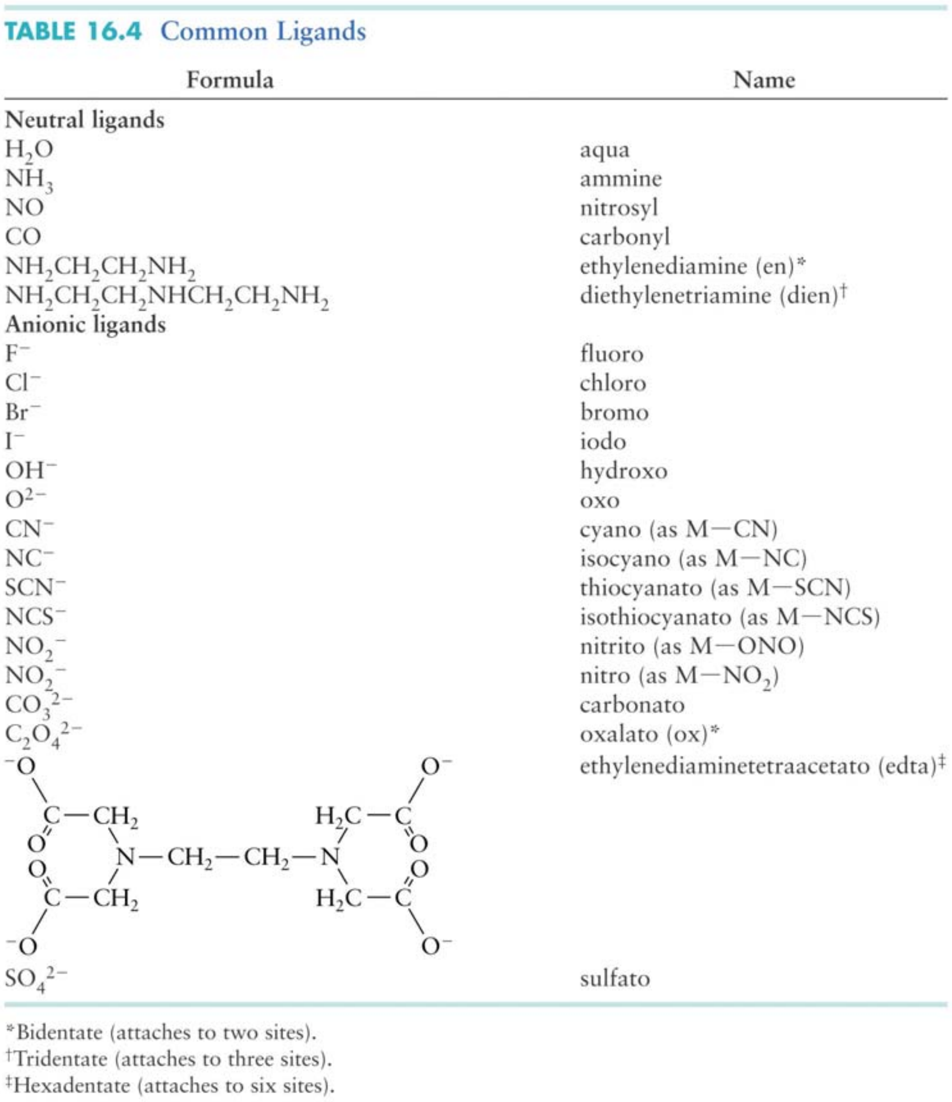


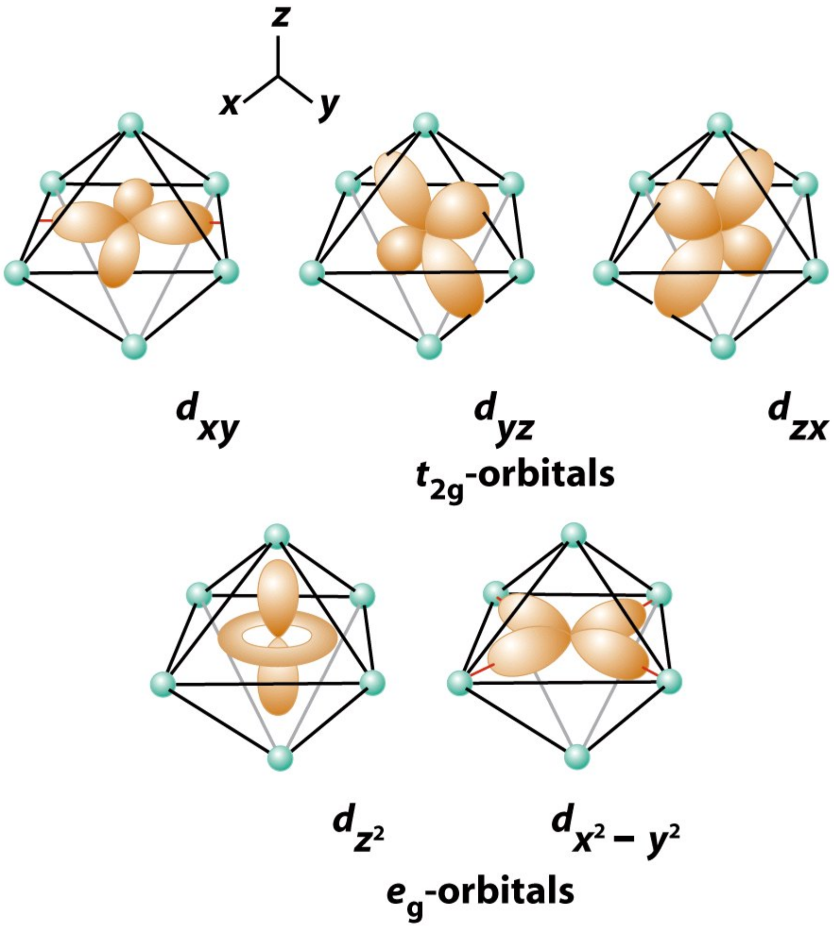
TABLE 16.4 Common Ligands

Formula	Name
Neutral ligands	
H_2O	aqua
NH_3	ammine
NO	nitrosyl
CO	carbonyl
$NH_2CH_2CH_2NH_2$	ethylenediamine (en)*
$NH_2CH_2CH_2NHCH_2CH_2NH_2$	diethylenetriamine (dien)†
Anionic ligands	
F^-	fluoro
Cl^-	chloro
Br^-	bromo
I^-	iodo
OH^-	hydroxo
O^{2-}	oxo
CN^-	cyano (as M—CN)
NC^-	isocyano (as M—NC)
SCN^-	thiocyanato (as M—SCN)
NCS^-	isothiocyanato (as M—NCS)
NO_2^-	nitrito (as M—ONO)
NO_2^-	nitro (as M—NO_2)
CO_3^{2-}	carbonato
$C_2O_4^{2-}$	oxalato (ox)*
	ethylenediaminetetraacetato (edta)‡
SO_4^{2-}	sulfato

*Bidentate (attaches to two sites).
†Tridentate (attaches to three sites).
‡Hexadentate (attaches to six sites).

The Electronic Structure of Complexes

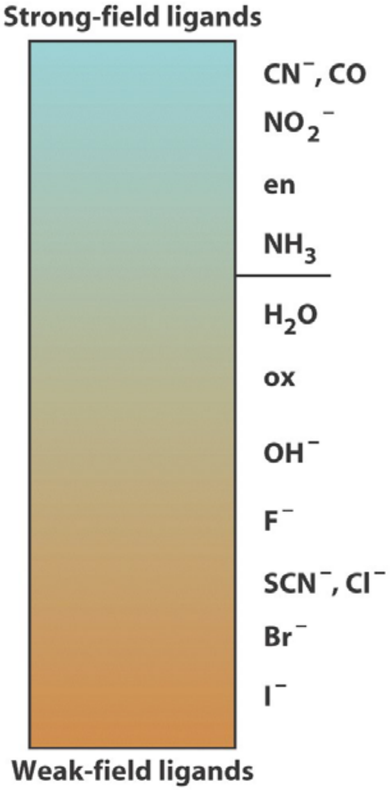
Crystal Field Theory



In crystal field theory one assumes that the ligands can be represented by negative point charges and that the metal is a positive point charge located at the center of the system. One then examines how these negative point charges interact with the *d* orbitals

The Electronic Structure of Complexes

Spectrochemical Series



Different ligands affect the *d* orbitals of a given metal atom or ion to different degrees and thus produce different values of the ligand field splitting. The spectrochemical series arranges ligands according to the relative magnitudes of the ligand field splitting that they produce.

The Electronic Structure of Complexes

Electron Configurations

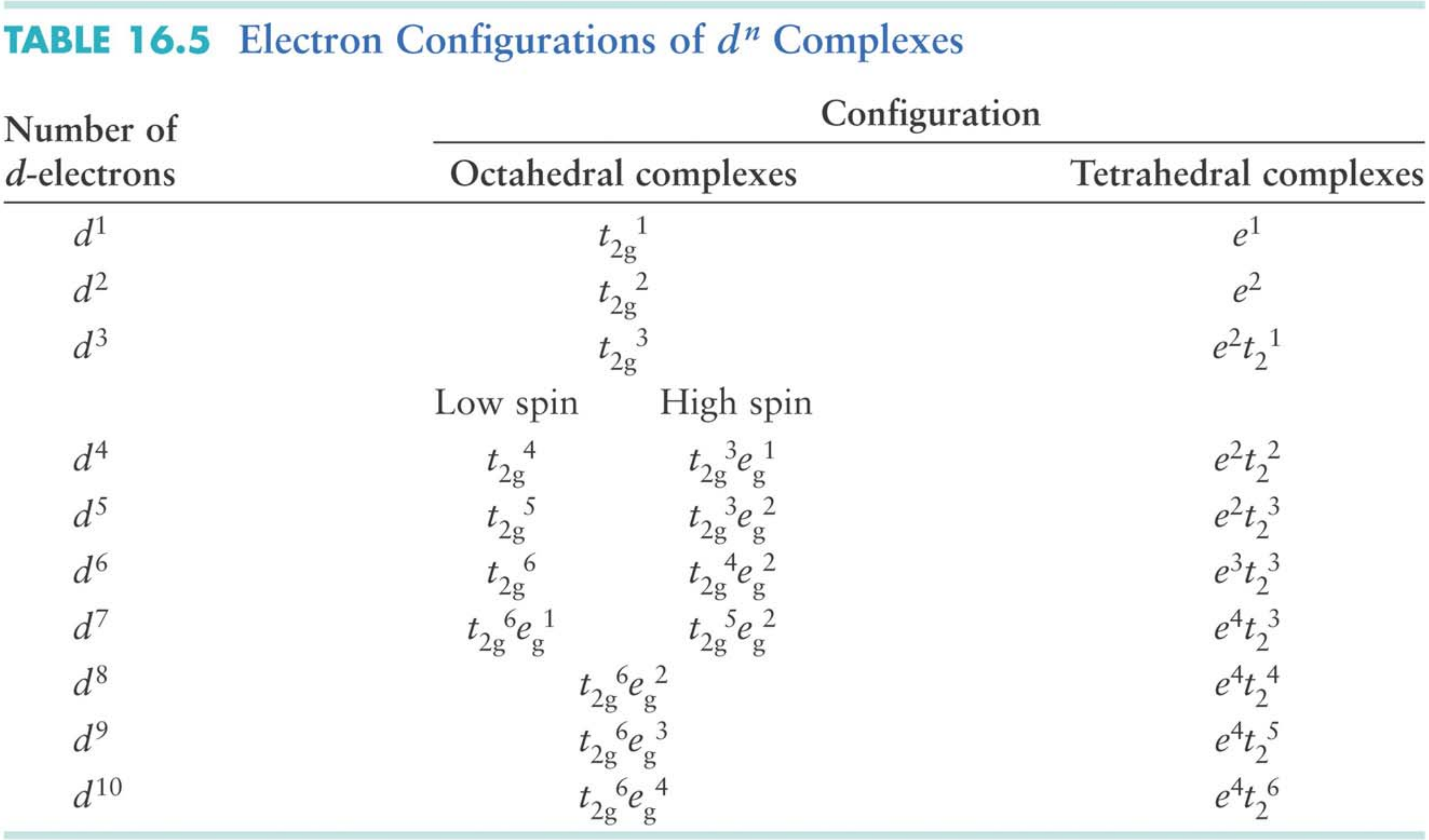
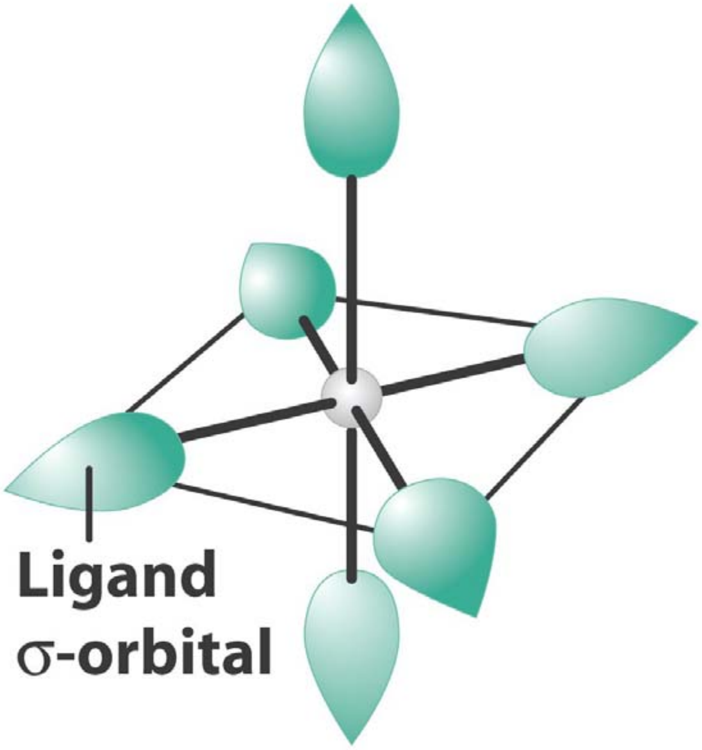


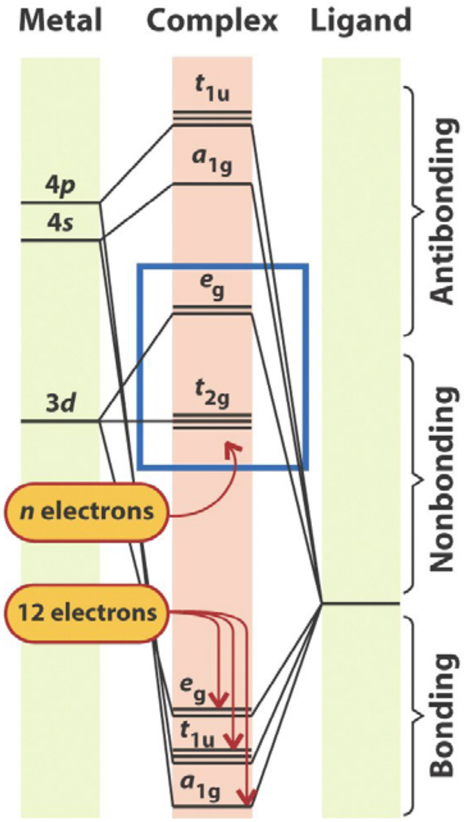
TABLE 16.5 Electron Configurations of d^n Complexes

Number of *d*-electrons	Configuration: Octahedral complexes, Low spin	Octahedral complexes, High spin	Tetrahedral complexes
d^1	$t_{2g}{}^1$		e^1
d^2	$t_{2g}{}^2$		e^2
d^3	$t_{2g}{}^3$		$e^2t_2{}^1$
d^4	$t_{2g}{}^4$	$t_{2g}{}^3e_g{}^1$	$e^2t_2{}^2$
d^5	$t_{2g}{}^5$	$t_{2g}{}^3e_g{}^2$	$e^2t_2{}^3$
d^6	$t_{2g}{}^6$	$t_{2g}{}^4e_g{}^2$	$e^3t_2{}^3$
d^7	$t_{2g}{}^6e_g{}^1$	$t_{2g}{}^5e_g{}^2$	$e^4t_2{}^3$
d^8	$t_{2g}{}^6e_g{}^2$		$e^4t_2{}^4$
d^9	$t_{2g}{}^6e_g{}^3$		$e^4t_2{}^5$
d^{10}	$t_{2g}{}^6e_g{}^4$		$e^4t_2{}^6$

The Electronic Structure of Complexes

Ligand Field Theory



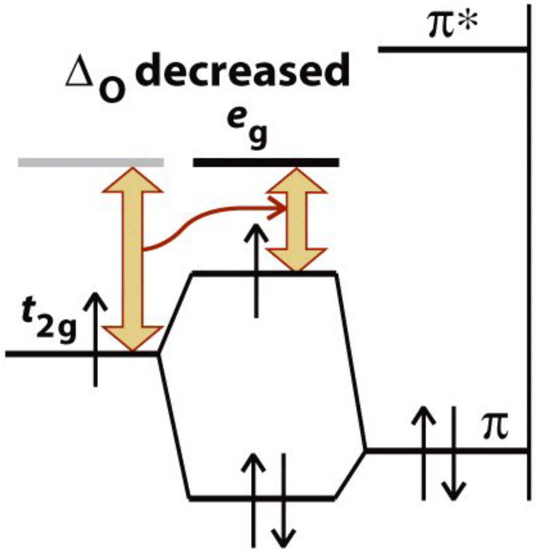


Only one orbital is considered for the ligands. 9 orbitals come from the *d*-metal, 6 orbitals come from the ligands making a total of 15 molecular orbitals. The electrons from the ligands fill up all of the bonding orbitals, leaving the electrons from the metal to fill the nonbonding and antibonding orbitals.

The Electronic Structure of Complexes

Ligand Field Theory

Weak Field Ligand

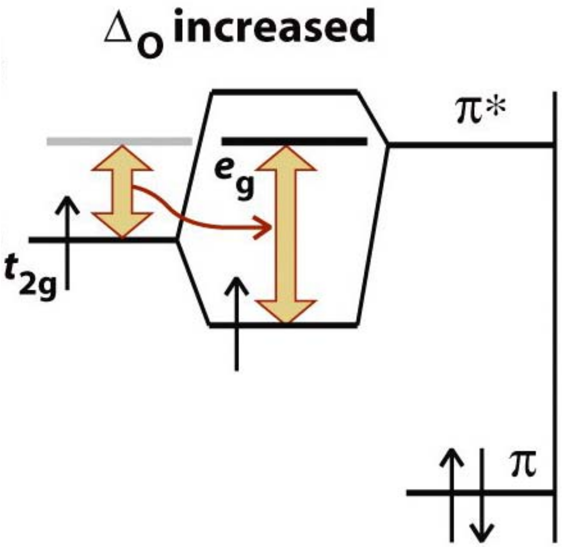


If the t_{2g} orbital is closer in energy to the π bonding orbital, the two orbitals will interact and the electron in the filled π orbitals will enter the lower energy molecular orbital therefore the electrons in the *d*-metal will have to occupy the higher energy molecular orbital which will decreases the octahedral field splitting. This is what happens for weak field ligands.

The Electronic Structure of Complexes

Ligand Field Theory

Strong Field Ligand



If however the t_{2g} orbitals are closer in energy to the π antibonding orbital when the two orbitals interact, there are no electrons from the ligand to go into the lower energy molecular orbital. Therefore the electrons in the metal can enter the lower energy orbital and the octahedral field splitting will increase. This is what happens for strong field ligands.