

Coordination Compounds: Bonding

- Let us first think about, what a good theory should be able to do in general. The answer is, that it should be able to make many correct explanations for experimental observations based on a few, sensible, assumptions. *A satisfactory theory of bonding in coordination compounds* must account for properties such as **color** and **magnetism**, as well as **stereochemistry** and **bond strength**.
- No single theory as yet does all this for us. Rather, several different approaches have been applied to transition metal complexes. There are essentially three bonding concepts that are used to describe the bonding in coordination compounds: **Crystal Field Theory (CFT)**, **Valence Bond Theory (VBT)**, and **Ligand Field Theory (LFT)**.

Crystal Field Theory (CFT)

- The major theory is the crystal field theory. It is actually not a bonding theory because it is based on repulsive electrostatic interactions. It was originally developed to explain color in ionic crystals. Later, it was found that it can also explain colors in molecular coordination compounds and is suitable to explain shapes and magnetism of complexes. However, because it is based on repulsive electrostatic interactions it cannot actually explain what holds the

atoms in a molecule together. However, the crystal field theory is quite simple and convenient to use, and there is a lot of practicality to it.

- ✓ In 1929, J. Becquerel proposed that the **central metal ion in a transition-metal complex was subject to an electrostatic field originating from the surrounding ligands**. In transition metal ions, we need to focus on how the electrons in the ***d orbitals*** of a metal ion are affected when they are in a complex. In the same year, Hans Albrecht Bethe used symmetry and group theory to place Becquerel's idea on the firm theoretical foundation we now call CF theory. Just three years later, in 1932, John Hasbrouck Van Vleck (1899–1980) demonstrated the power of the new theory when he interpreted the paramagnetism of the first-row transition-metal complexes and the rare earths with good quantitative accuracy. Van Vleck and his co-workers made many other seminal contributions to the development of the theory and its applications over the following decade.

□ Valence Bond Theory

- The valence bond concept was introduced by Linus Pauling in 1931 to explain covalent bonding in molecules of main group elements. A **valence bond approach** to the problem was introduced in the 1940s by Linus Pauling, but it *proved less successful* than the CF theory in the interpretation of electronic spectra.
- The basic idea is to overlap half-filled valence orbitals to form covalent bonds in which the two electrons are shared between the bonding partners (Fig. 7.1.1).

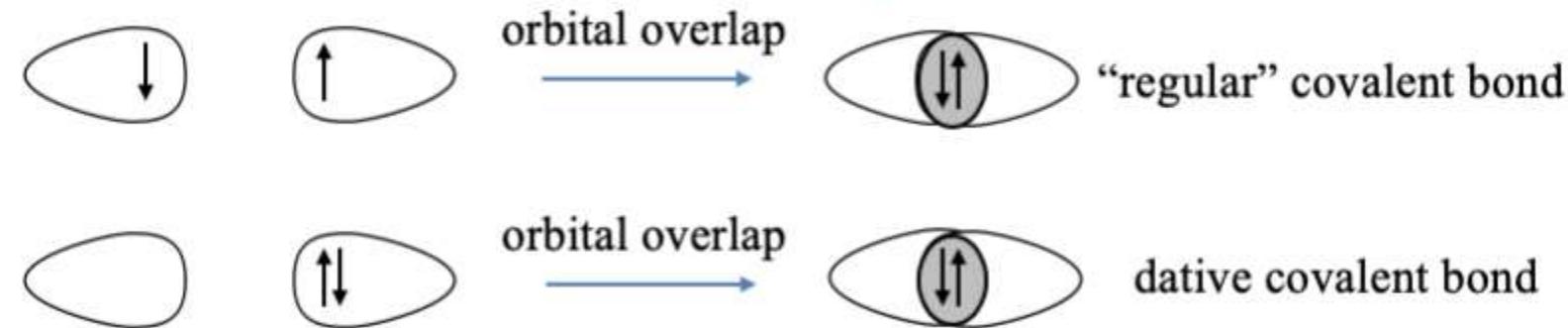


Figure 7.1.1 Electron sharing and valence bond theory

- These orbitals can either be atomic orbitals or hybridized atomic orbitals. The concept works very well to explain the shapes of molecules of main group elements. The valence bond concept in its original form assumes that each bonding partner contributes one electron to

the covalent bond. This is not consistent with the dative bonding in coordination compounds where it is assumed that one partner donates an electron pair and the other partner accepts it. To adapt valence bond theory to suit coordination compounds, Pauling suggested that a dative bond is formed via the overlap of a full valence orbital of the donor and an empty valence orbital of the acceptor. We will see that this concept can explain the shapes of coordination compounds in some cases, but overall it does not work very well. We will also see that valence bond theory can explain magnetism in some cases, but also here the valence bond theory has significant deficits. By its nature, valence bond theory cannot explain optical properties. Overall, valence bond theory is far more suitable for main group element molecules compared to transition metal complexes.

□ Ligand Field Theory

- The third theory is the ligand field theory. It is the most powerful theory, but also the most complicated one. Basically, it is ***molecular orbital theory*** applied to coordination compounds. It can make detailed statements about the number of bonds and shapes of molecules and can explain the magnetism and optical properties of coordination compounds.
- With the growth of the ***molecular orbital (MO) theory*** in the second half of the 20th century, the time appeared ripe to tackle the most obvious shortcoming of the CF theory.

➤ The *interaction between ligand and central metal ion is clearly more than a purely electrostatic one*; there is also *a significant element of covalency* which should be amenable to a MO treatment. The range of theories which grew from this seed carries the collective name of ***ligand field theory***. *Modifications of the simple crystal field theory that take into account such factors as the partial covalency of the metal-ligand bond are called ligand field theory*. This term is often used to signify both the purely electrostatic crystal field theory and its modifications.

Table 20.1 Electron Configurations and Other Properties of the First-Row Transition Metals

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Electron configuration									
M	$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$
M^{2+}	—	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$
M^{3+}	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$
Electronegativity	1.3	1.5	1.6	1.6	1.5	1.8	1.9	1.9	1.9
Ionization energy (kJ/mol)									
First	631	658	650	652	717	759	760	736	745
Second	1235	1309	1413	1591	1509	1561	1645	1751	1958
Third	2389	2650	2828	2986	3250	2956	3231	3393	3578
Radius (pm)									
M	162	147	134	130	135	126	125	124	128
M^{2+}	—	90	88	85	80	77	75	69	72
M^{3+}	81	77	74	64	66	60	64	—	—
Standard reduction potential (V)*	-2.08	-1.63	-1.2	-0.74	-1.18	-0.44	-0.28	-0.25	0.34

*The half-reaction is $M^{2+}(aq) + 2e^- \longrightarrow M(s)$ (except for Sc and Cr, where the ions are Sc^{3+} and Cr^{3+} , respectively).

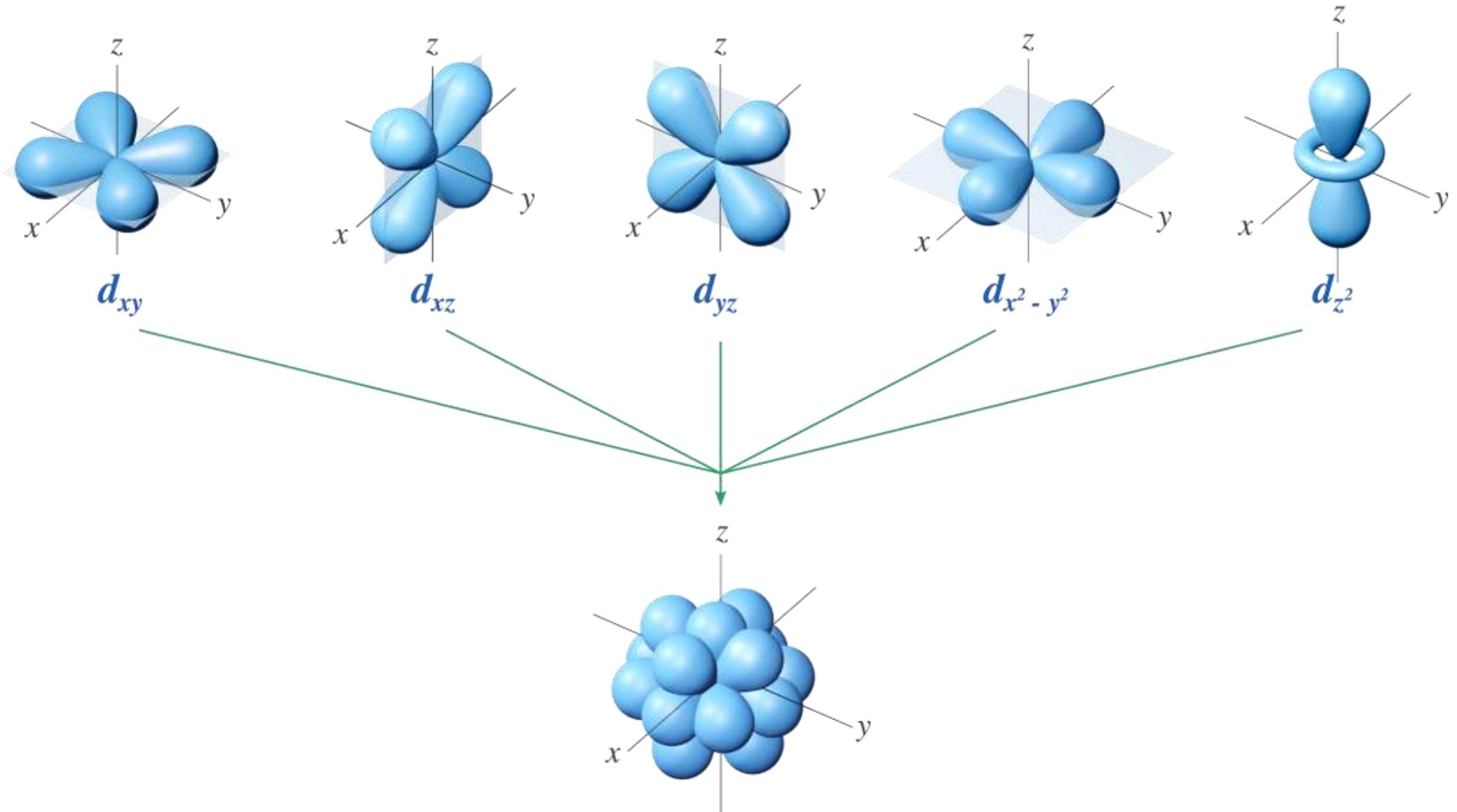


Figure 1.16.2: d orbitals.

Valence bond (VB) model

- Valence bond (VB) model is a localized bonding model for covalent bonds.
- Because the coordinate covalent bond is simply a sub-set of covalent bonding, it might be reasonable to begin a discussion of the bonding in coordination compounds by employing a VB approach.

Octahedral Complexes

- Because most coordination compounds have the octahedral geometry, we begin with the *σ-bonding formed using the six bond vectors* depicted in Figure 16.2.
- The *six σ-donating ligands will have maximum overlap with the three p-orbitals*, which also lie along the coordinate axes; the $d_{x_2-y_2}$ orbital, which has its lobes along the x and y axes; the d_{z^2} orbital, which has its larger lobe lying along the z axis and the donut region in the xy plane; and, of course, the spherically symmetric s-orbital.
- **The hybridization of an octahedral coordination compound is d^2sp^3 .** The results match our chemical intuition because the ligands in an octahedral coordination geometry lie along the x, y, and z coordinate axes.

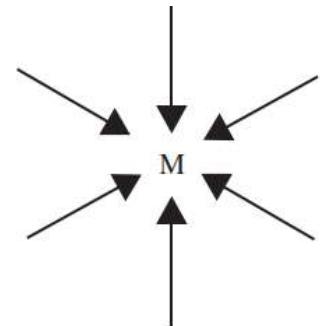
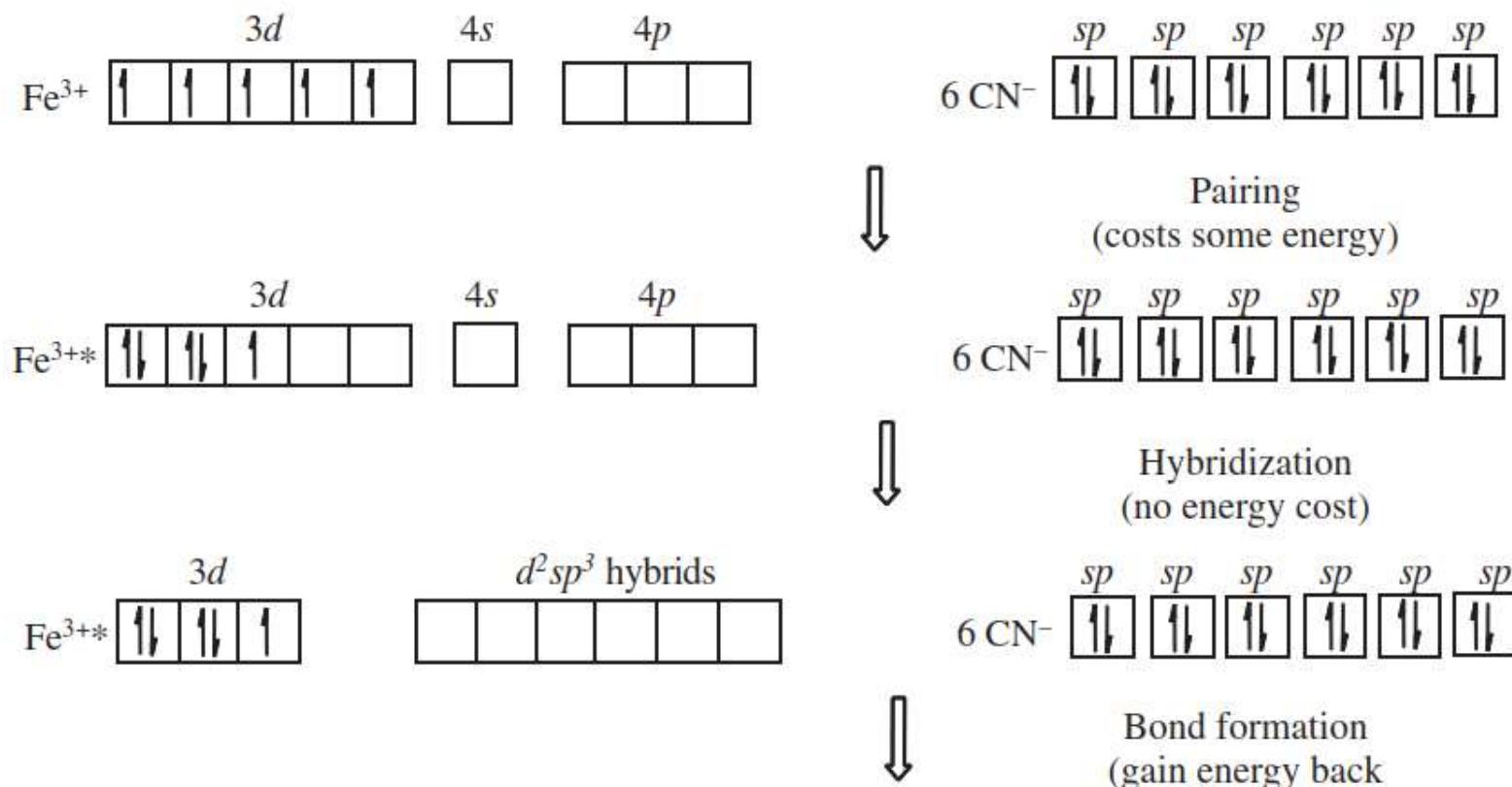


FIGURE 16.2 Bond vector basis set for the hybridization of a metal ion (M) in an octahedral coordination geometry.

- The VB development for $[\text{Fe}(\text{CN})_6]^{3-}$ is shown in Figure 16.3.
- Each of the empty $d^2\text{sp}^3$ hybrid orbitals on the Fe^{3+} ion can accept a pair of electrons from one of the sp hybrid orbitals on the CN^- ligands to form the six $\text{Fe}-\text{CN}$ coordinate covalent bonds.



- Can we also explain the **magnetism** of the molecule?
- How many unpaired electrons are there in the complex ion?

FIGURE 16.3 Valence bond treatment for the $[\text{Fe}(\text{CN})_6]^{3-}$ ion.

MAGNETIC MEASUREMENTS

Key points: *Magnetic measurements are used to determine the number of unpaired spins in a complex* and hence to identify its ground-state configuration.

- Compounds are classified as **diamagnetic** if they are **repelled** by a magnetic field and **paramagnetic** if they are **attracted** by a magnetic field. The two classes are distinguished experimentally by magnetometry.
- The **magnitude of the paramagnetism** of a complex is commonly reported in terms of the **magnetic dipole moment** it possesses: the higher the magnetic dipole moment of the complex, the greater the paramagnetism of the sample.
- In a free atom or ion, both the **orbital** and **the spin angular momenta give rise to a magnetic moment** and contribute to the paramagnetism. The following formula for the magnetic moment (μ) of a molecule in Bohr magnetons is:

$$\mu_{\text{total}} = -[\{L(L + 1)\} + 4\{S(S + 1)\}]^{1/2} \mu_B$$

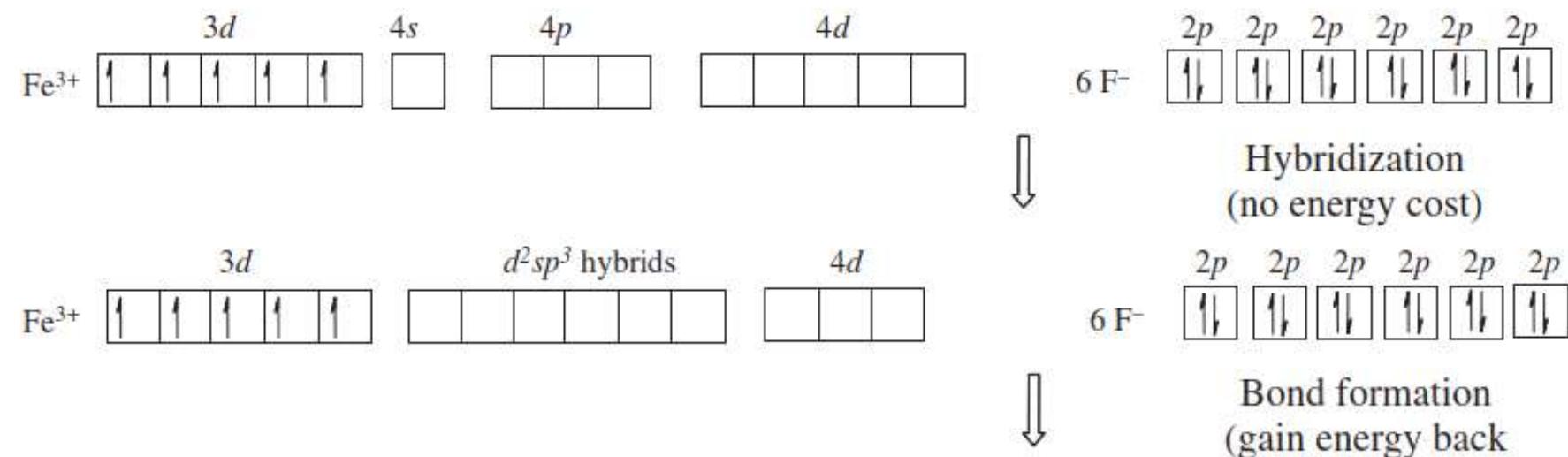
- where μ_B is the Bohr magneton, $\mu_B = e\hbar/2m_e$ with the value $9.274 \times 10^{-24} \text{ J T}^{-1}$.
- When **the atom or ion is part of a complex**, any **orbital angular momentum is normally quenched**, or **suppressed**, as a result of the interactions of the electrons with their nonspherical environment. However, if any electrons are unpaired, **the net electron spin angular momentum survives** and gives rise to **spin-only paramagnetism**, which is characteristic of many d-metal complexes. The spin-only magnetic moment, μ , of a complex with total spin quantum number S is:

$$\mu = 2\{S(S + 1)\}^{1/2} \mu_B \quad (20.1)$$

- If N is the number of unpaired electrons each with spin $s = 1/2$, then **$S = N/2$** ,

$$\mu = \{N(N + 2)\}^{1/2} \mu_B \quad (20.2)$$

- The calculated magnetic moment value 1.73 BM of the ferricyanide ion *is in reasonable agreement with the experimental value 2.20 BM.*
- **One problem** with the VB model is that ***not every Fe³⁺ coordination compound has the same magnetic properties.***
- For example, *the experimental magnetic moment of [FeF₆]³⁻ (5.85BM) is more consistent with five unpaired electrons than it is with one electron.*
- The **only way to rationalize** the magnetic behavior of [FeF₆]³⁻ is to use the VB development shown in Figure 16.4, where the 3d electrons remain unpaired and *the much higher lying 4d orbitals are used in the construction of the six d²sp³ hybrids (i.e., sp³d²).*
- Clearly, this is **not** a very satisfying model.



- **How many unpaired electrons are there in the complex ion?**

FIGURE 16.4 Valence bond treatment for the $[FeF_6]^{3-}$ ion.

VBT: Octahedral d⁵ **High Spin** and **Low Spin** Orbital Complex

➤ The valence bond theory has also difficulties to explain so-called **high spin** and **low spin octahedral complexes**. For example, it is known from magnetic measurements for 3d transition metal ions that they can make octahedral complexes with either one unpaired electron or five unpaired electrons, depending on the ligand. In the first case, the number of paired electrons in the d-orbitals is maximized, and we have a low-spin complex, in the other case the number of unpaired electrons is maximized, and we have a high spin complex. What approach does valence bond theory take to explain this phenomenon?

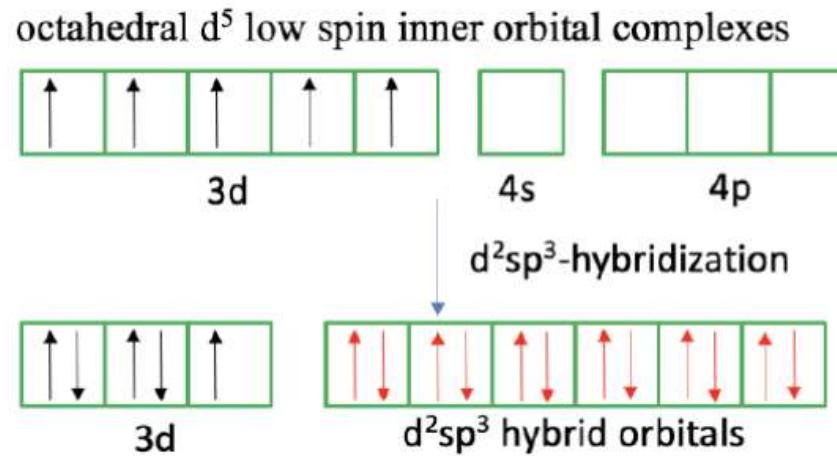


Figure 7.1.5 Valence bond theory applied to an octahedral d⁵ **low spin-complex**

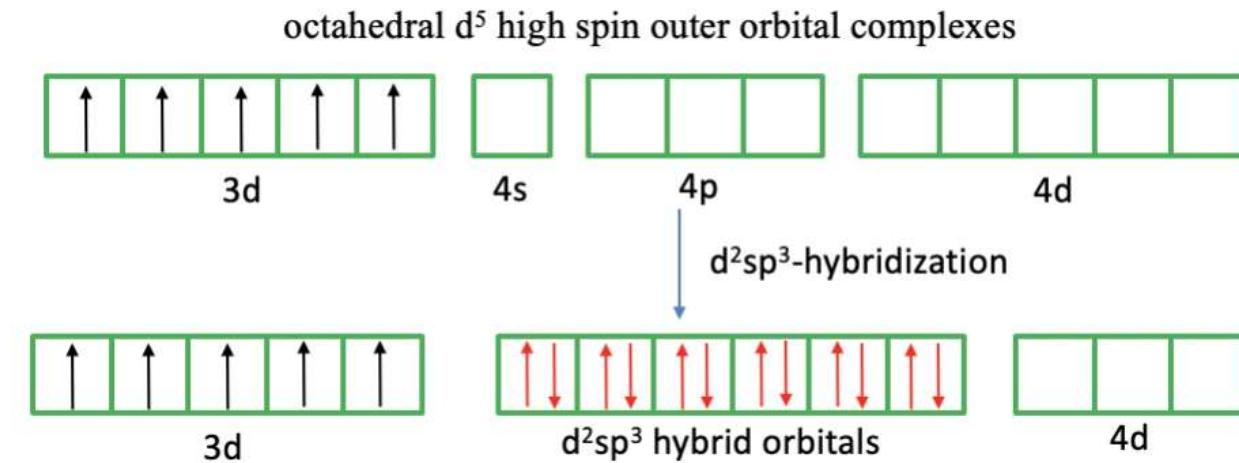


Figure 7.1.6 Valence bond theory applied to an octahedral d⁵ **high spin-complex**

➤ In the case of a low spin-complex, valence bond theory assumes a so-called inner orbital complex. Like in the square planar complex it is assumed that unpaired electrons reverse their spins and move into other half-filled d-orbitals so that spin-pairing is maximized. In the case of a d⁵ ion, two electrons reverse their spin, and move into two other half-filled orbitals. This leaves one unpaired electron. We see that due to the movement of the two electrons two 3d-orbitals are empty now, and so are the 4s and the 4p orbitals. The six empty orbitals can now be combined to form d²sp³-hybridized orbitals that can explain the octahedral shapes.

- Approaching the ligands overlaps the electron lone pair at the ligand with the empty hybrid orbitals to form a dative, covalent bond. We can also say the ligands donate electron lone pairs to form six covalent bonds. We can again criticize that ***spin-reversal is forbidden*** and ***spin-pairing is energetically unfavorable*** making the approach valence bond theory takes to explain the low-spin complex unsatisfactory.
- What about the 3d high spin complex (Fig. 7.1.6)? In this case we cannot pair spins to create empty d-orbitals because we need to explain five unpaired electrons. Now, valence bond theory makes another new assumption. It assumes that the outer 4d orbitals get involved in the bonding. These orbitals are empty and available for hybridization. We can therefore hybridize the 4s, the three 4p and two 4d, orbitals to form sp^3d^2 hybridized orbitals. In the last step we can approach the ligands, and the ligands can donate their electron lone pairs into the transition metal d-orbitals. Now we have explained the six bonds, the octahedral shape, and the five unpaired electrons.
- We can again critique the valence bond approach. What justification is there to assume that the 4d orbitals are involved. The answer is: Very little. These orbitals are just too high in energy to be considered valence orbitals. It is not reasonable to assume that they are involved in the bonding. Therefore, again, we see that valence bond theory has difficulties to explain the properties of a complex. Valence bond theory also does not explain distortions of octahedral complexes due to the Jahn-Teller effect.

VBT: Octahedral d⁷ High and Low Spin Orbital Complex

- High-spin and low-spin complexes are not only observed for octahedral complexes of d⁻-ions, but for example also for octahedral d⁷ ion complexes. A low-spin complex has three unpaired electrons and a high-spin complex has one unpaired electron. We will see that valence bond theory has even greater troubles to explain these compounds.

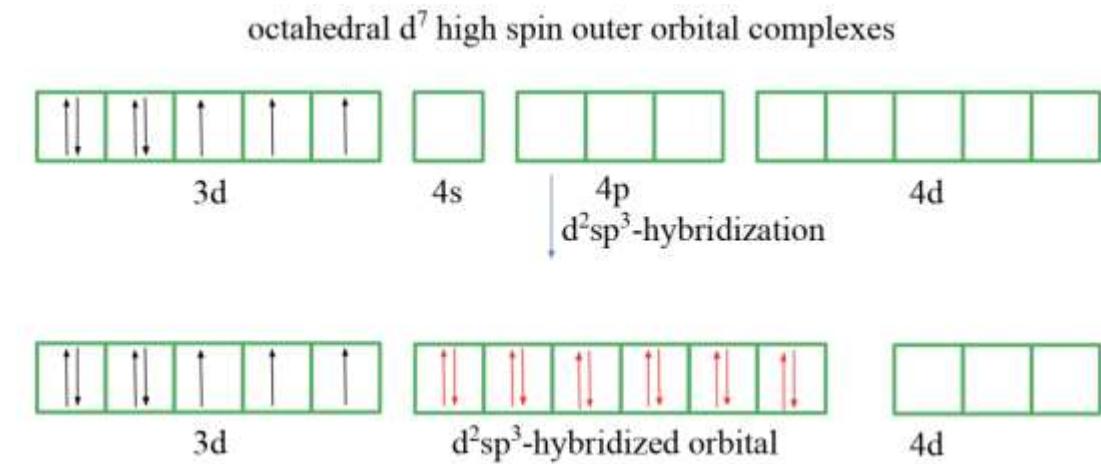
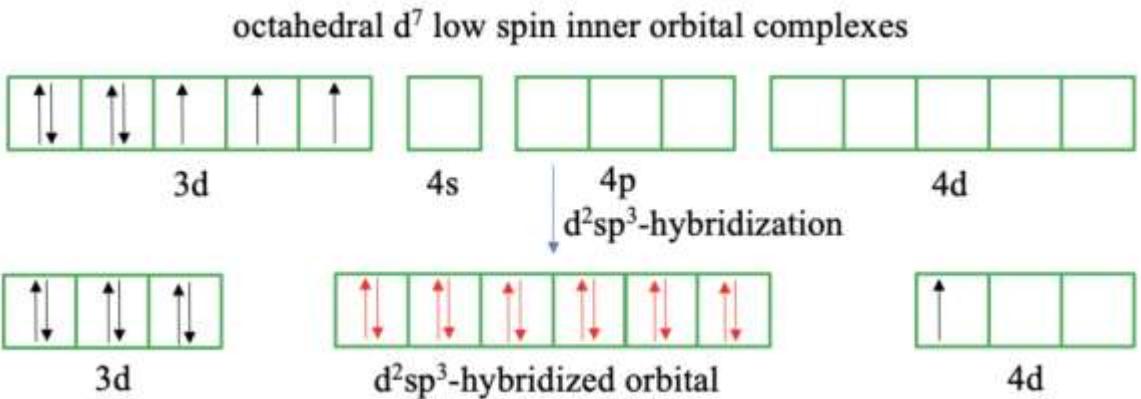


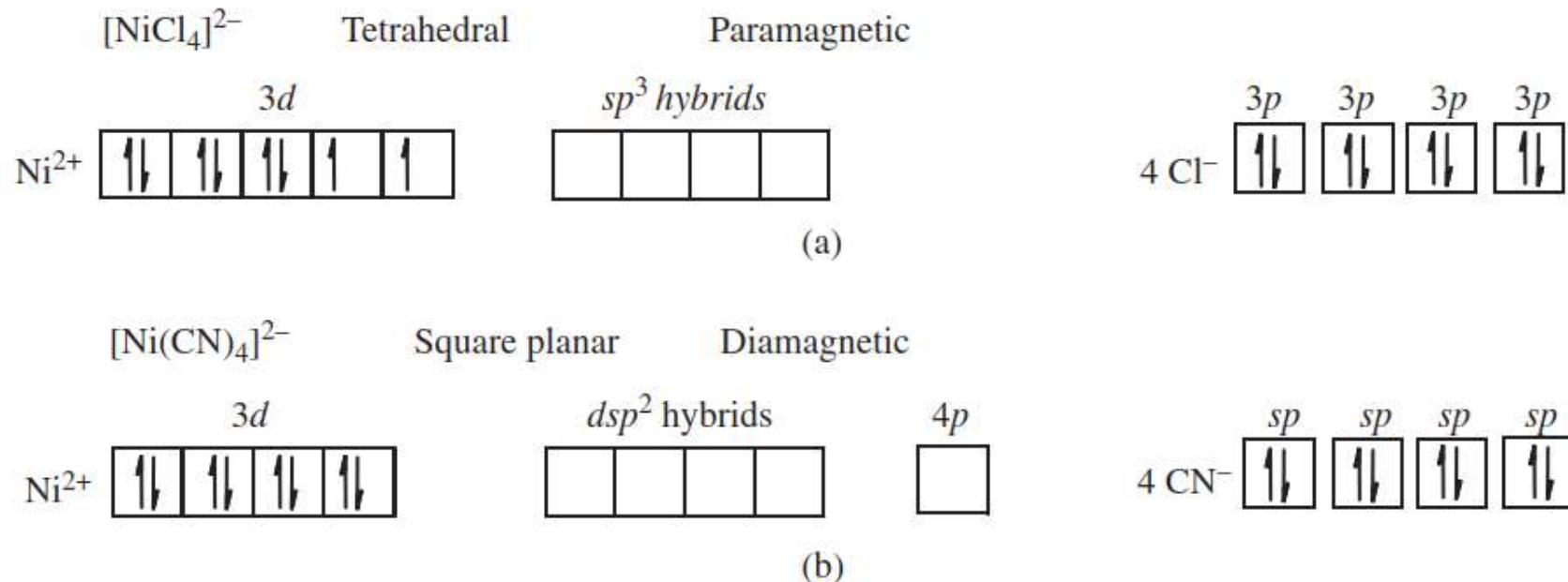
Figure 7.1.7 Valence bond theory applied to an octahedral d⁷ **low spin-complex**

Figure 7.1.8 Valence bond theory applied to an octahedral d⁷ **high spin-complex**

- In a d⁷ ion there are four paired and three unpaired electrons according to Hund's rule (Fig. 7.1.7). We can reverse the spin of one unpaired electron and pair it with an unpaired electron in another half-filled orbital to reduce the number of unpaired electrons to one. However, this gives us only one empty 3d orbital available for d²sp³-hybridization. In this case we cannot produce more empty 3d-orbitals by reversing the spin. Therefore, we must make again the questionable assumption that outer orbitals are involved in the bonding such as the 4d orbitals. Valence bond theory now suggests to move the unpaired electron from the 3d to the 4d orbital. This is simply done to create another empty 3d orbital that we need for d²sp³-hybridization. However, why would the 3d electron just go into another orbital of much higher energy? If we make this questionable assumption though, we have indeed six orbitals available for hybridization, and we can let the ligands donate an electron pair into the empty hybrid orbitals.

- Finally, let us discuss an octahedral d⁷ high-spin outer orbital complex (Fig. 7.1.8). In this case we cannot pair any spins in the 3d orbitals. Therefore, we assume again that the 4d orbitals get involved in the bonding, and hybridize two of them with the 4s and the three 4p orbitals. The six ligands can then donate six electron pairs into the orbitals thereby creating six bonds and explaining the octahedral shape.
- Overall, we see that ***in the valence bond theory we move around electrons as we please in order to explain shapes and magnetism of complexes without good justification***. Therefore, the valence bond theory, while extremely valuable for main group compounds, is only of limited use for transition metal complexes.
- *Another shortcoming of the VB model is its inability to predict the geometry of four-coordinate compounds.*
- ✓ For example, the [NiCl₄]²⁻ ion is **tetrahedral** and **paramagnetic**, while the **isoelectronic** [Ni(CN)₄]²⁻ and [PtCl₄]²⁻ ions are **square planar** and **diamagnetic**.
- The VB treatment for the two different cases is shown in Figure 16.5.
- As we know, tetrahedral compounds are sp³ hybridized, while square planar (D_{4h}) compounds are d_{x²-y²}sp² hybridized.
- Another obvious problem with the VB model is that ***it fails to explain the diverse colors, electronic spectra, and photoelectron spectroscopy*** of coordination compounds.
- Thus, the *VB theory is of little use in coordination chemistry*, and it is included here only for historical purposes.

FIGURE 16.5 Valence bond treatment for $[\text{NiCl}_4]^{2-}$ (a) and $[\text{Ni}(\text{CN})_4]^{2-}$ (b).



➤ How many unpaired electrons are there in the complex ions?

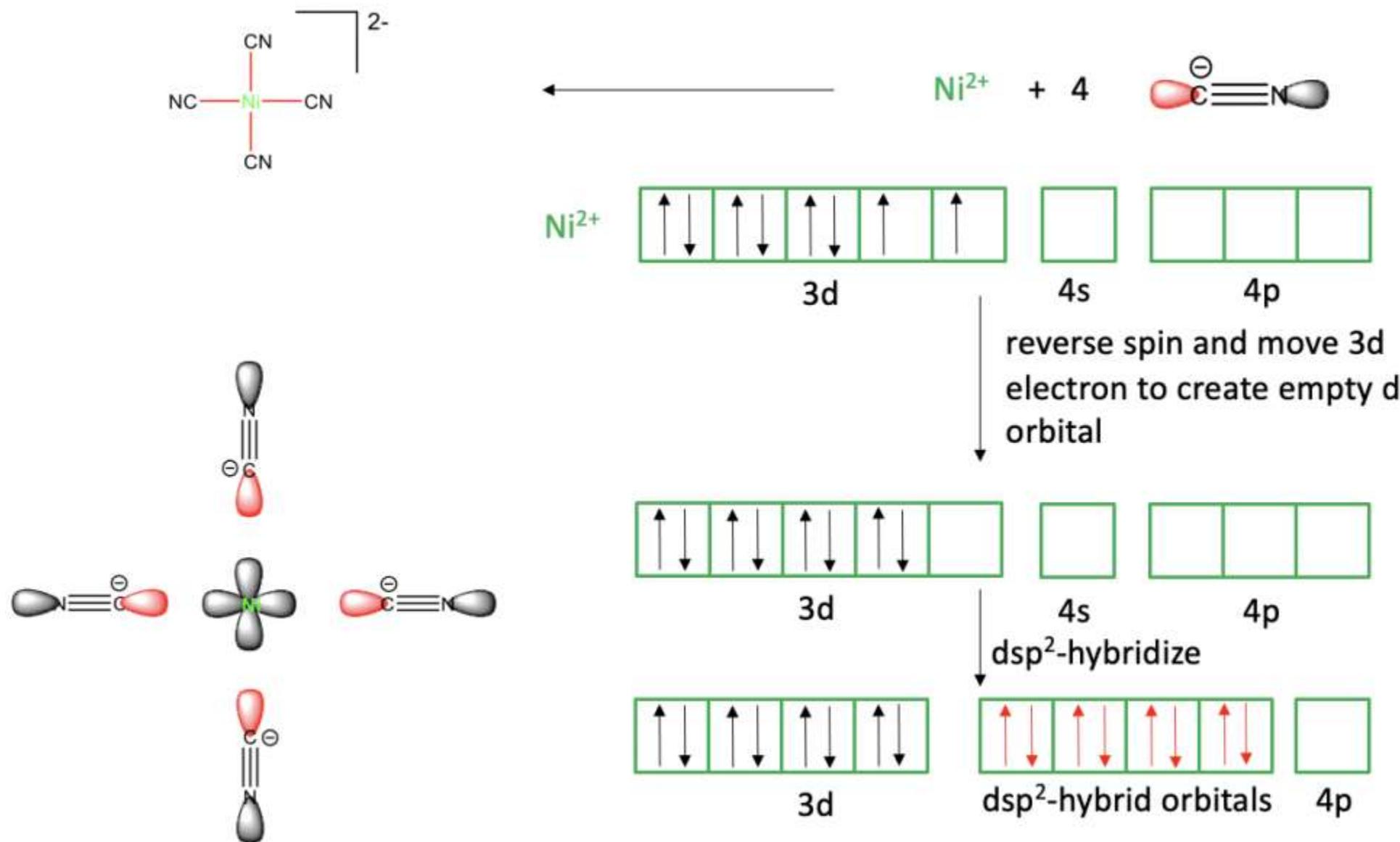


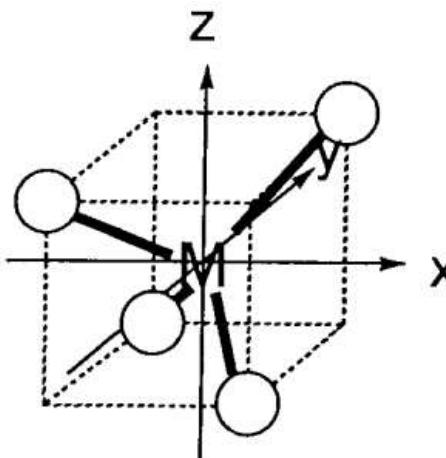
Figure 7.1.4 Valence bond theory applied to the tetracyanoniobate (2-) square planar complex

- In the valence bond picture we view the Ni-CN bonds as dative bonds, and the complex is considered an adduct of Ni^{2+} and CN^- .
- To explain the four bonds, the Ni ion would need to have four empty valence orbitals. Ni is a group 10 metal and a neutral Ni atom has the electron configuration $4s^23d^8$. To create a Ni^{2+} ion we must remove the two 4s electrons, and thus the Ni^{2+} has the electron configuration $3d^8$. Do we have four empty orbitals available? Yes, the 4s and the three 4p orbitals are empty but again they are not equivalent and thus not suitable to explain four equivalent Ni-C bonds. Can we hybridize these orbitals? Yes, we can, but the resulting four sp^3 hybridized orbitals would **not be suitable** to explain the square planar shape, only the tetrahedral shape.
- To explain its diamagnetic square planar geometry, what valence bond theory suggests in this case is to reverse the spin of one of the unpaired d electrons and move it into the other half-filled d-orbital. This produces an empty d-orbital that we can now hybridize with the 4s and two of the 2p orbitals to four dsp^2 -hybridized orbitals. These four orbitals have the property that their lobes point toward the vertices of a square, thus they are suitable to explain the square-planar shape. We can approach the ligands now on the bond axes to create orbital overlap between the empty dsp^2 Ni and the electron lone pairs of the ligands. We can also say that the ligands donate their electron lone pairs into the hybridized metal orbitals. This produces the four covalent bonds that we need and yields a molecule of a square planar shape.
- We can see that the valence bond theory can still explain the square planar shape, but only with the help of the additional assumption that one of the d-electrons gets spin-reversed and moves into another d-orbital. An assumption a theory makes should always be reasonable, so let us critique how reasonable this assumption is. Firstly, is the spin-reversal reasonable? Spin-reversal is a quantum-mechanically forbidden process, and thus it is questionable to assume that it happens. Secondly, there is no good explanation for why the electron moves. The energy of two spin-paired electrons in the same orbital is actually higher than that of two spin-paired electrons in different orbitals. So overall, we see that valence bond theory has difficulties to explain the square planar shape. It must make assumptions that are not very plausible.

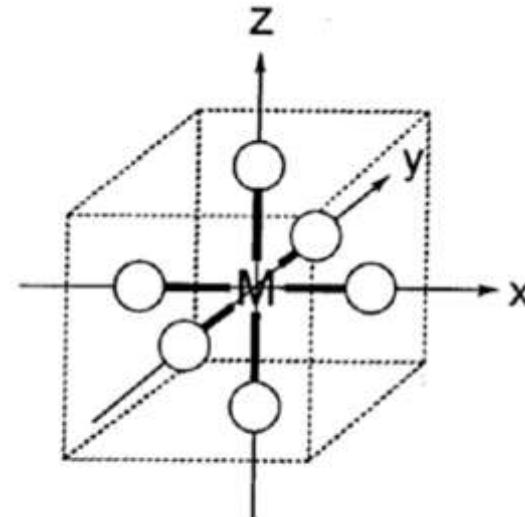
CRYSTAL FIELD THEORY

- The VB model of chemical bonding developed is incapable of explaining the magnetic properties of coordination compounds, the preference of some metals for square planar over tetrahedral coordination, and the rich electronic spectra of coordination compounds.
- As a result of its many shortcomings, an alternative model called *crystal field theory* (CFT) was proposed by the physicist Hans Bethe in 1929. Originally developed to explain the electronic transitions in colored minerals, CFT takes a completely electrostatic (ionic) approach.
- What are the principles of crystal field theory? **Crystal field theory assumes that the *electrons in the metal d-orbitals are surrounded by an electric field which is caused by the ligand electrons*.** This electric field is called the **crystal field**. The name crystal field comes from the fact that this principle was first applied to transition metal ions surrounded by anions in crystals and was only later extended to transition metal ions surrounded by ligands in molecular coordination compounds. The assumption that ligands surrounding a transition metal ion produce an electric field makes sense because the ligands contain electrons that are associated with an electric field. It is further assumed that the crystal field raises the energy of the metal-d-orbitals because of electrostatic repulsion between the ligand electrons and the metal electrons.
- According to this model, the metal ion can be represented as a sphere of positive charge at the center of the coordination compound (or occupying one of the cationic sites in a crystalline lattice), while the ligands behave as negative point charges distributed around the metal ion with the appropriate coordination geometry.
- The ***crystal field theory focuses on the repulsions*** between *ligand electrons* and *d electrons* of the central ion.
- In the presence of ligands, because repulsions exist between ligand electrons and *d* electrons, the ***d-orbital energy levels of the central metal ion are raised***. As we will soon see, however, ***they are not all raised to the same extent***.

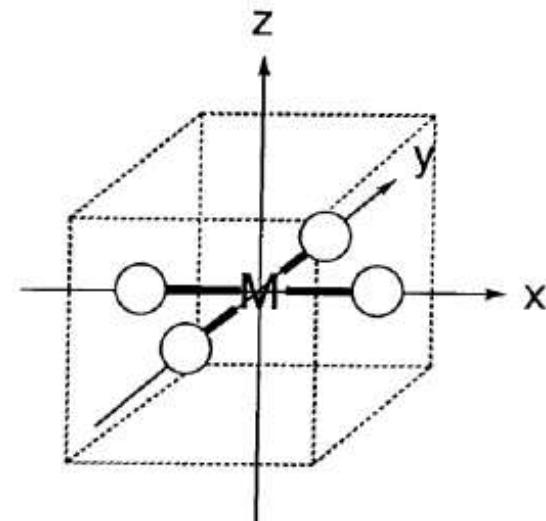
- The interaction of a free metal ion in the gas phase with a sphere of negative charge causes the energy of the *d*-orbitals to increase as a result of the smaller value of *r*.
- All five of the *d* orbitals are **alike in energy** when in an **isolated atom or ion**, but they are **unlike in their spatial orientations**.
- ✓ One of them, is directed along the *z* axis, and another, has lobes along the *x* and *y* axes. The remaining three have lobes extending into regions between the perpendicular *x*, *y*, and *z* axes.
- ✓ According to the **crystal-field model**, the energies of the *d*-orbitals are a function of the ***relative positions of the ligands and the d-orbitals***.
- ✓ Therefore, the energy of the *d*-orbitals depend on the ligand orientations around the central metal ion/atom.



tetrahedral coordination



octahedral coordination



square planar coordination

Figure 6.2.5: Ligand positions in the Cartesian coordinate with a metal ion at the origin.

□ Octahedral Crystal Field: Splitting of d Orbitals in an Octahedral Field of Ligands

- Let us first consider the case for the *most common coordination geometry of octahedral*.
- The crystal field (CF) treatment of the problem is developed in Figure 22.22, which shows what happens to the energies of the degenerate set of *d*-orbitals when an imaginary sphere of negative charge is introduced to a positively charged transition metal cation in the gas phase.
- In the first step, the energies of all the *d*-orbitals are raised as the distance separating the charges (*r*) in the denominator of Coulomb's law decreases ($Q^+Q^-/4\pi\epsilon_0 r$).
- In the next step, the sphere of negative charge is divided by six (ligands) and placed into specific sites around the metal ion in the positions where the ligands lie. *For octahedral coordination, these negative point charges lie along the positive and negative directions of the three Cartesian axes.*
- ✓ Since the value of *r* has not changed in this second step (it simply involved a redistribution of the negative charge), the overall energy of the *d*-orbitals remains unchanged by this second perturbation. However, the degeneracy of the orbitals is removed, as some of the orbitals lie closer to the negative point charges than others.
- When the orbitals are filled with electrons (donated by six ligands approaching/binding the metal ion), the repulsion between electrons in the *d*-orbitals and the negative point charges representing the ligands in the crystal will cause some of the orbitals to be raised in energy. Let's follow the orientation of ligand and orbital and how the approach affects orbital energies.
- Six ligands approaching a metal ion along the mutually perpendicular *x*, *y*, and *z* axes, which form an octahedral arrangement (Figure 22.22). The spatial arrangement of *d*-orbitals in the octahedral configuration of 6 ligands shows that the ligands are aligned along the *x*, *y*, and *z* axes and interact *most strongly* with electrons in the 2 orbitals that also are aligned along the axes and *not so strongly* with electrons in the 3 orbitals that are aligned between the axes.

- Because the $d_{x^2-y^2}$ and d_z^2 orbitals have **lobes that point directly at the negative point charges** as shown in Figure 22.22, they **will be raised in energy** as a result of electron-electron repulsions. The d_{xy} , d_{xz} , and d_{yz} orbitals in an octahedral CF have their lobes **pointed between the coordinate axes** and **away from** the negative point charges. Because the total energy of the d-orbitals must remain unchanged by this second step, the energies of the remaining three d-orbitals must be lowered relative to the barycenter.
- Thus, the **five d-orbitals will split into two different sets** in an octahedral CF. $d_{x^2-y^2}$ and d_z^2 orbitals are to be **raised** with respect to the barycenter, while d_{xy} , d_{xz} , and d_{yz} orbitals are **stabilized**.
- According to the Group theory, an octahedral complex belongs to the point group O_h and in the point group O_h the $d_{x^2-y^2}$ and d_z^2 -orbitals are degenerate and have e_g symmetry. Therefore, the higher lying, doubly degenerate set of orbitals, $d_{x^2-y^2}$ and d_z^2 -orbitals in an octahedral crystal field are also often just called the **e_g -orbitals**. The energy of remaining d-orbitals, d_{xy} , d_{xz} , and d_{yz} is reduced by exactly the same amount. These orbitals are triple-degenerate in the point group O_h and have the symmetry type t_{2g} . Thus, these d-orbitals in an octahedral crystal field are also often called the **t_{2g} -orbitals**.

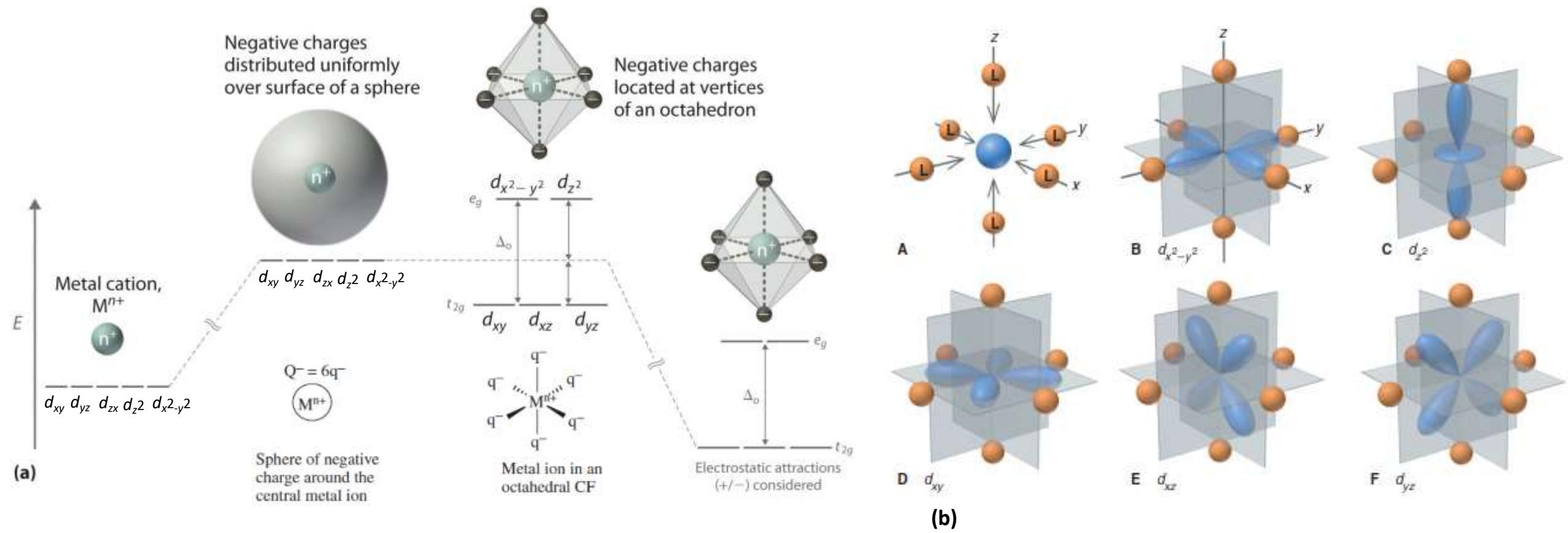


Figure 22.22. (b) The five d orbitals in an octahedral field of ligands. Orange balls: Ligands. A: Ligands approach along the x , y , and z axes. B and C: The $d_{x^2-y^2}$ and d_{z^2} orbitals point directly at some of the ligands. D to F: The d_{xy} , d_{xz} , and d_{yz} orbitals point between the ligands. In an isolated atom, these orbitals have the same energy. However, in an octahedral complex, the orbitals split into two sets, with the d_{z^2} and $d_{x^2-y^2}$ orbitals having higher energy than the other three. The repulsion is greater in the case of the d_{z^2} and $d_{x^2-y^2}$ orbitals.

□ Splitting of d Orbitals in an Octahedral Field of Ligands: *CF splitting Energies*

- The crystal field model explains that the **properties of complexes result from the splitting of d-orbital energies**, which arises from electrostatic attractions between the metal cation and the negative charge of the ligands. This *negative charge is either partial, as in a polar covalent ligand like NH₃, or full, as in an anionic ligand like Cl⁻*.
- The **energy difference between the t_{2g} and the e_g orbitals is called the crystal field splitting energy, Δ_o or 10 Dq.**
- The energy of the t_{2g} orbitals is decreased by 2/5Δ_o relative to the spherical crystal field, and the energy of the e_g-orbitals is increased by 3/5Δ_o relative to the spherical crystal field.
- Where do the factors 2/5 and 3/5 come from? They are due to the law of the conservation of energy. The overall energy reduction due to the energy decrease of the t_{2g}-orbitals must be equal to the overall energy increase due to the energy increase of the e_g orbitals: $\Sigma E(t_{2g}) = - \Sigma E(e_g)$. Because there are three t_{2g} orbitals but only two e_g orbitals this equation only holds when the energy of the e_g orbitals is increased by 3/5Δ_o and the energy of the t_{2g} orbitals is decreased by 2/5Δ_o, or 3x 2/5Δ_o = 2 x 3/5 Δ_o. Note that the energy of all orbitals will be greater in comparison to the case of no electrical field existing, but the energy is increased to a greater extent for the e_g-orbitals compared to the t_{2g} orbitals.

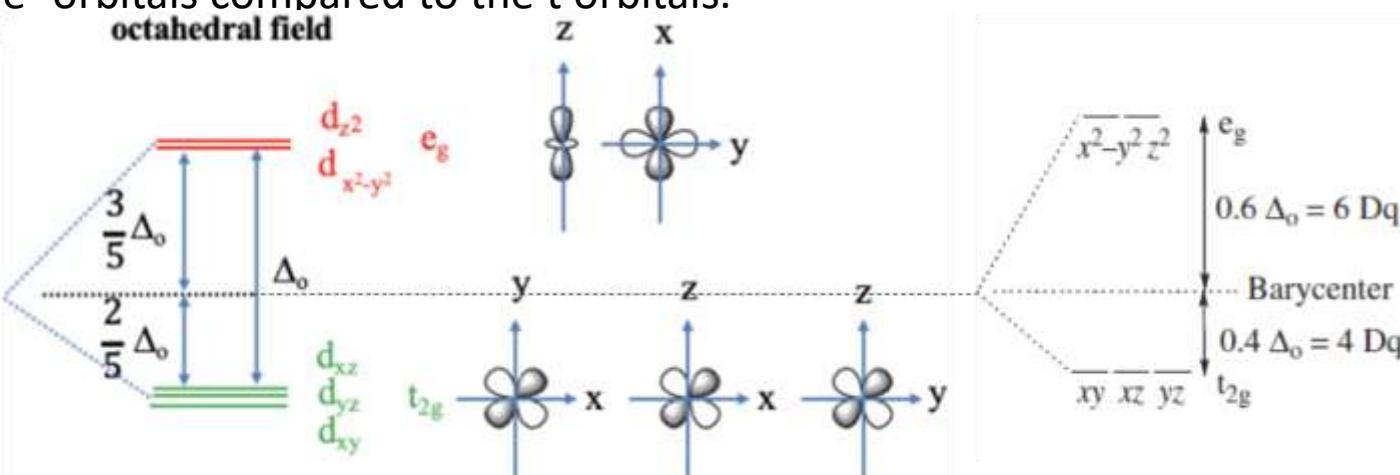


FIGURE 16.6 The interaction of a free metal ion in the gas phase with a sphere of negative charge causes the energy of the d-orbitals to increase as a result of the smaller value of *r*.

Crystal field splitting energy (Δ)

- The splitting of orbital energies is called the *crystal field effect*, and the energy difference between e_g and t_{2g} orbitals is the **crystal field splitting energy (Δ)**.
- *Different ligands create crystal fields of different strength:*
 - **Strong-field ligands** lead to a *larger splitting energy* (larger Δ).
 - **Weak-field ligands** lead to a *smaller splitting energy* (smaller Δ).
- ✓ For instance, H_2O is a *weak-field ligand*, and CN^- is a *strong-field ligand* (Figure 22.18). Note the different orbital occupancies; we discuss the reason for these differences shortly.

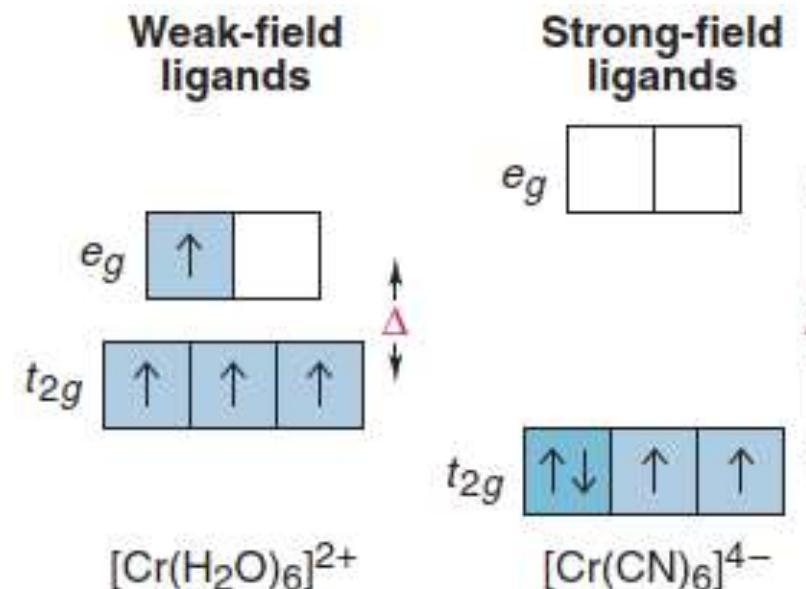
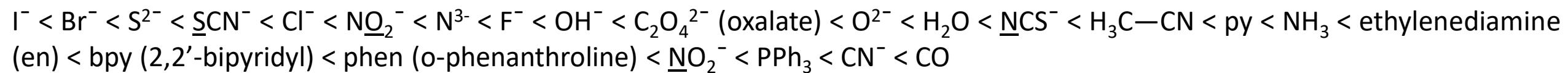


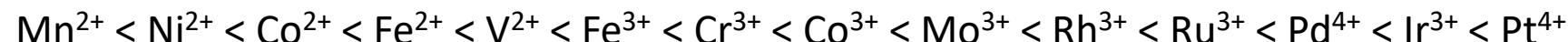
Figure 22.18 The effect of ligands and splitting energy orbital occupancy.

- Importantly, the **magnitude of Δ** , which can be *measured spectroscopically* (for d-d transitions), depends on **the identity and charge of the metal ion**, as well as **the type of ligand**. By characterizing a range of different ligands, a **spectrochemical series** can be established which lists the ligands in the order of increasing Δ :



← weak field – strong field →

- Given the same geometry of coordination and identical ligands, the crystal field splitting Δ for different *metals* increases in the following order (approximately):



← weak field – strong field →

- The **value of Δ_0 increases with an increasing oxidation state of the central metal ion** (compare the two entries for Fe and Co) and **increases down a group** (compare, for instance, the locations of Co, Rh, and Ir). The *variation with oxidation state reflects the smaller size of more highly charged ions and the consequently shorter metal-ligand distances and stronger interaction energies*. The *increase down a group reflects the larger size of the 4d and 5d orbitals compared with the compact 3d orbitals and the consequent stronger interactions with the ligands*.

☐ Low-Spin and High-Spin Complexes

❖ **Keypoint:** If the electron configurations for any d-electron count is different depending on Δ , the configuration with more paired electrons is called **low spin** while the one with more unpaired electrons is called **high spin**.

- The *magnitude of the crystal field splitting Δ can affect the electronic configuration*, and thus *the magnetic properties of a complex*; in particular, if there are several electrons populating the d orbitals, such as for example in Fe^{3+} .
- As illustrated in Fig. 11.11, electrons are filled into the orbitals according to the principles we have discussed earlier. One electron is added to each of the degenerate orbitals until each orbital has one electron with the same spin. In an octahedral complex, this works straightforwardly up to the third electron. *The fourth electron could either be placed as a paired electron in the lower set of d orbitals (**low-spin complex**) or as an unpaired electron in the energetically higher set of d orbitals (**high-spin complex**)*.
- Whether the **first** or **the second** scenario happens **depends on the magnitude of crystal field splitting energy (Δ) and the pairing energy**.

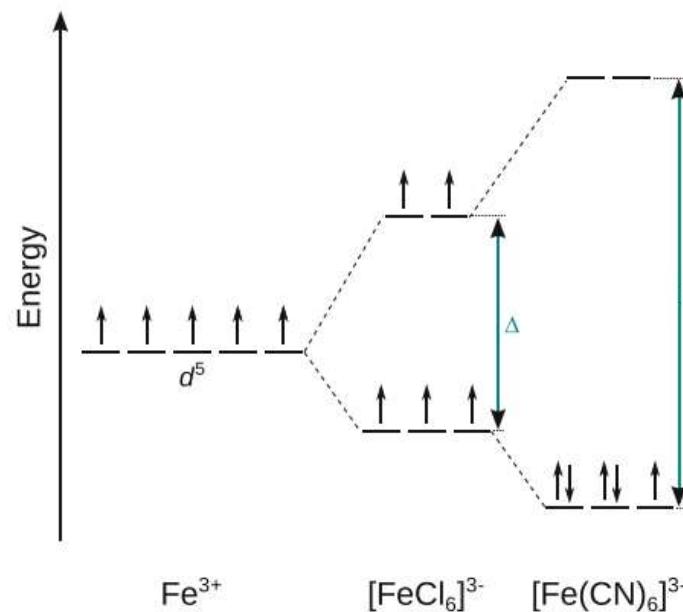


Fig. 11.11 Comparison of crystal field splitting for two Fe^{3+} complexes.

- One of the greatest strength of crystal field theory is that it can explain high-spin and low spin octahedral complexes in a simple way. The basis for that is the assumption that ***different ligands produce crystal fields of different strengths, and that the differently strong crystal fields produce different Δ_o values.*** This assumption is plausible because it can be expected that different ligands interact differently with a metal ion, for example, the bond length or the bond strength may be different. If the ligands produce a large crystal field then we would expect a large Δ_o , when the crystal field is small, then we would expect a small Δ_o .
- The ***size of the Δ_o determines if we get a high spin or a low spin complex.*** If the Δ_o is larger than the spin pairing energy, then a low spin complex is favored, if Δ_o is smaller than the spin-pairing energy, then the high spin complex is favored.

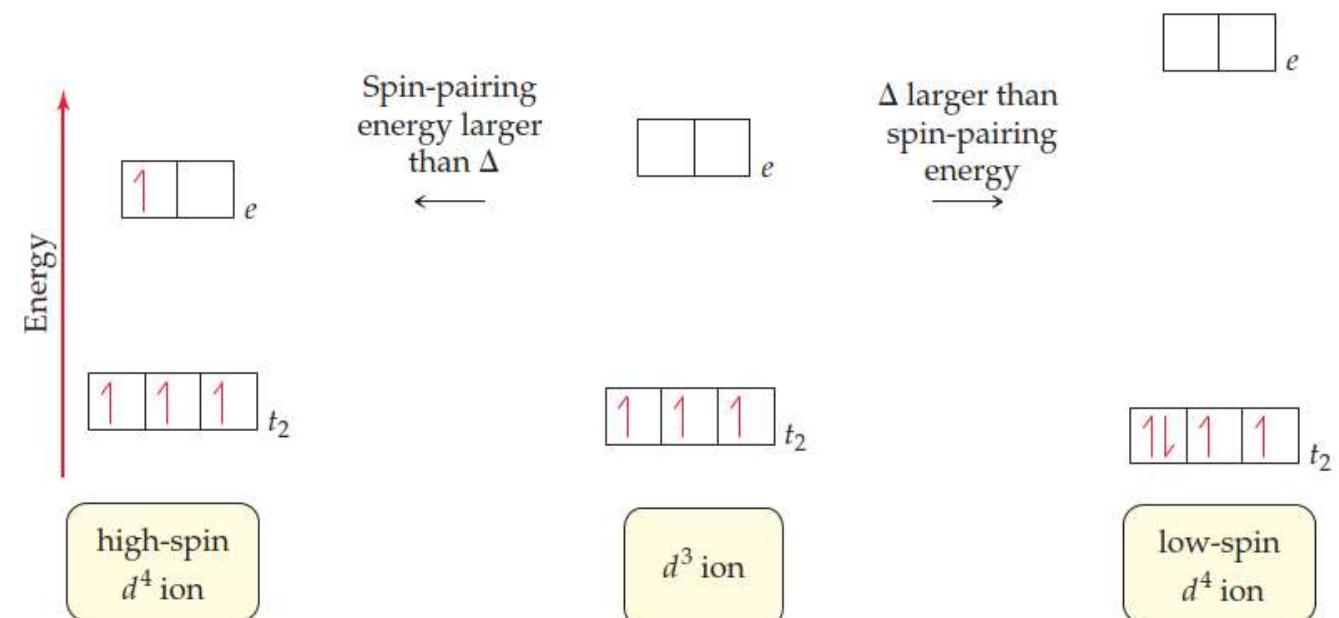


Figure 23.31 Two possibilities for adding a fourth electron to a d^3 octahedral complex. Whether the fourth electron goes into a t_2 orbital or into an e orbital depends on the relative energies of the crystal-field splitting energy and the spin-pairing energy.

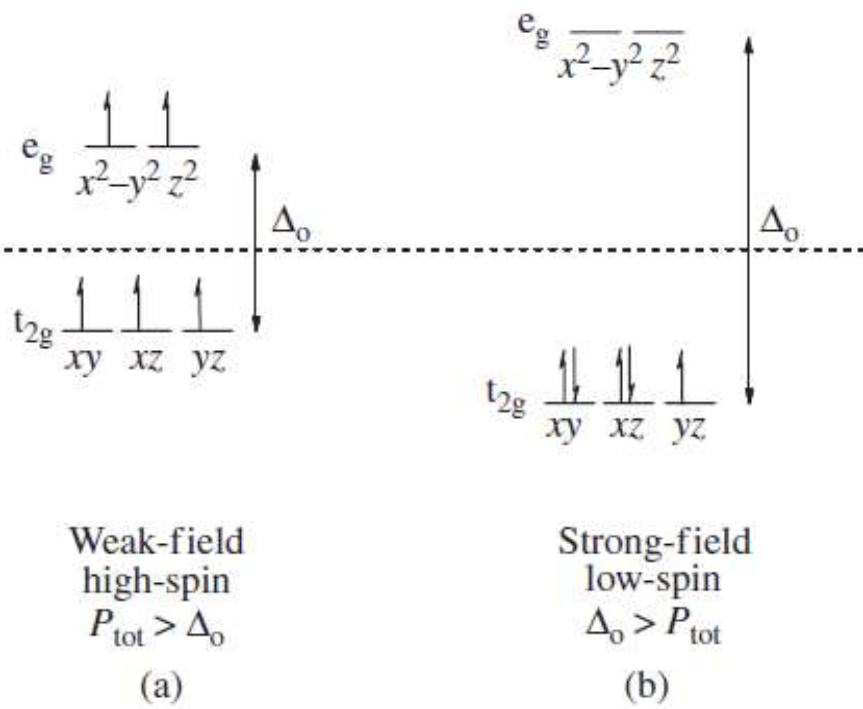


FIGURE 16.8

The relative energies of the five d -orbitals (a) in a weak CF and (b) in a strong CF. The dashed line represents the barycenter.

- As the valence d -electrons fill the empty orbitals in Figure according to the Aufbau principle, they will first populate the lower-lying t_{2g} set, going in with their spins paired according to Hund's rule.
- *Because the degenerate orbitals are indistinguishable, there is only one way to write the electron configurations for $d^1 - d^3$.*
- For the $d^4 - d^7$ electron configurations, however, there are two possible ways for the valence electrons in a metal to occupy the t_{2g} and e_g sets of orbitals.
- ✓ If the magnitude of $\Delta_0 > P_{\text{tot}}$ (where P_{tot} is the total spin pairing energy), *then the electrons will pair up first in a strong-field, low-spin (LS) configuration*, as shown in Figure here (16.18 (a)).
- ✓ If $P_{\text{tot}} > \Delta_0$, on the other hand, it will be easier for the electrons to *fill the upper e_g level before they pair up*, leading to the *weak-field, high-spin (HS) configuration* shown in Figure 16.8(b).

- Therefore, **high-spin complexes** are typically found with **metals/ligands at the weak-field end of the spectrochemical series** (such as e.g. $[\text{FeCl}_6]^{3-}$); vice versa, **low-spin complexes** are expected in complexes that comprise **metals and ligands at the high-field end** of the spectrochemical series (such as e.g. $[\text{Fe}(\text{CN})_6]^{3-}$).
- Since the formation of either a high-spin or a low-spin complex affects the pairing of electrons, the **crystal field splitting has repercussions in the magnetic properties** of a complex.
- Importantly, *with octahedral geometry, the options of forming either low-spin or high-spin complexes only exist for systems with 4–7 electrons in the d orbitals* (d^4 , d^5 , d^6 , d^7 complexes). For d^1 , d^2 d^3 and d^8 , d^9 , d^{10} complexes, there is only one possible electron configuration.
- In the electron configurations d^1 – d^3 all electrons are unpaired in the t_{2g} orbitals. Therefore, there is no electron that could be moved from t_{2g} to an e_g orbital.
- For the configurations d^8 – d^{10} all t_{2g} orbitals are necessarily full. Therefore, there is no possibility to move an electron from an e_g to a t_{2g} orbital regardless the crystal field strength.

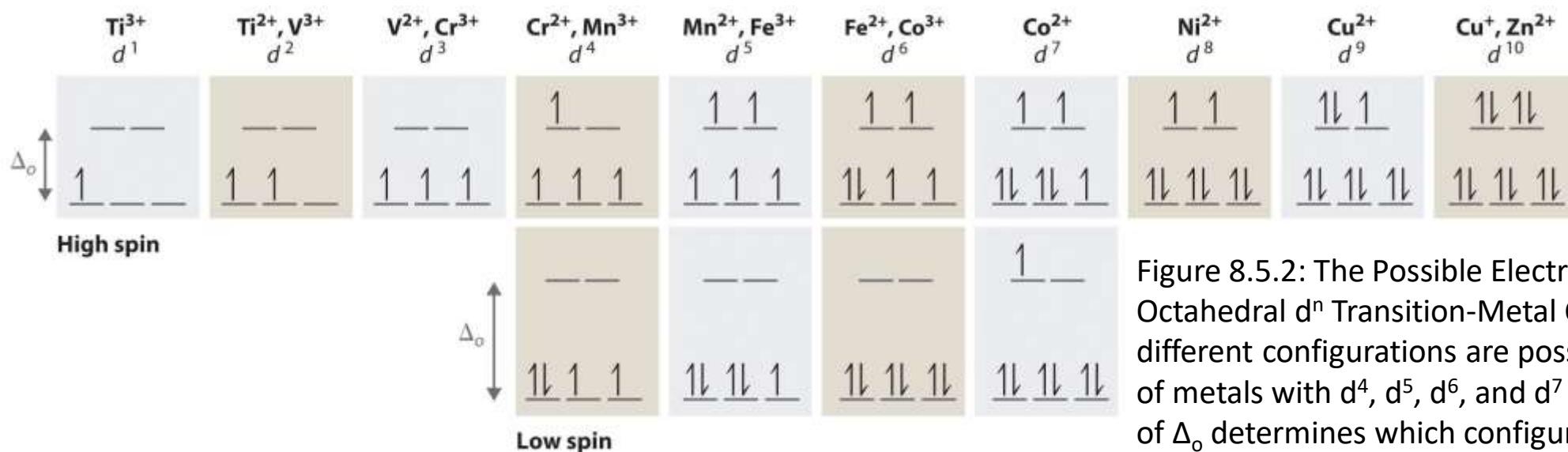


Figure 8.5.2: The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes ($n = 1$ – 10). Two different configurations are possible for octahedral complexes of metals with d^4 , d^5 , d^6 , and d^7 configurations; the magnitude of Δ_o determines which configuration is observed.

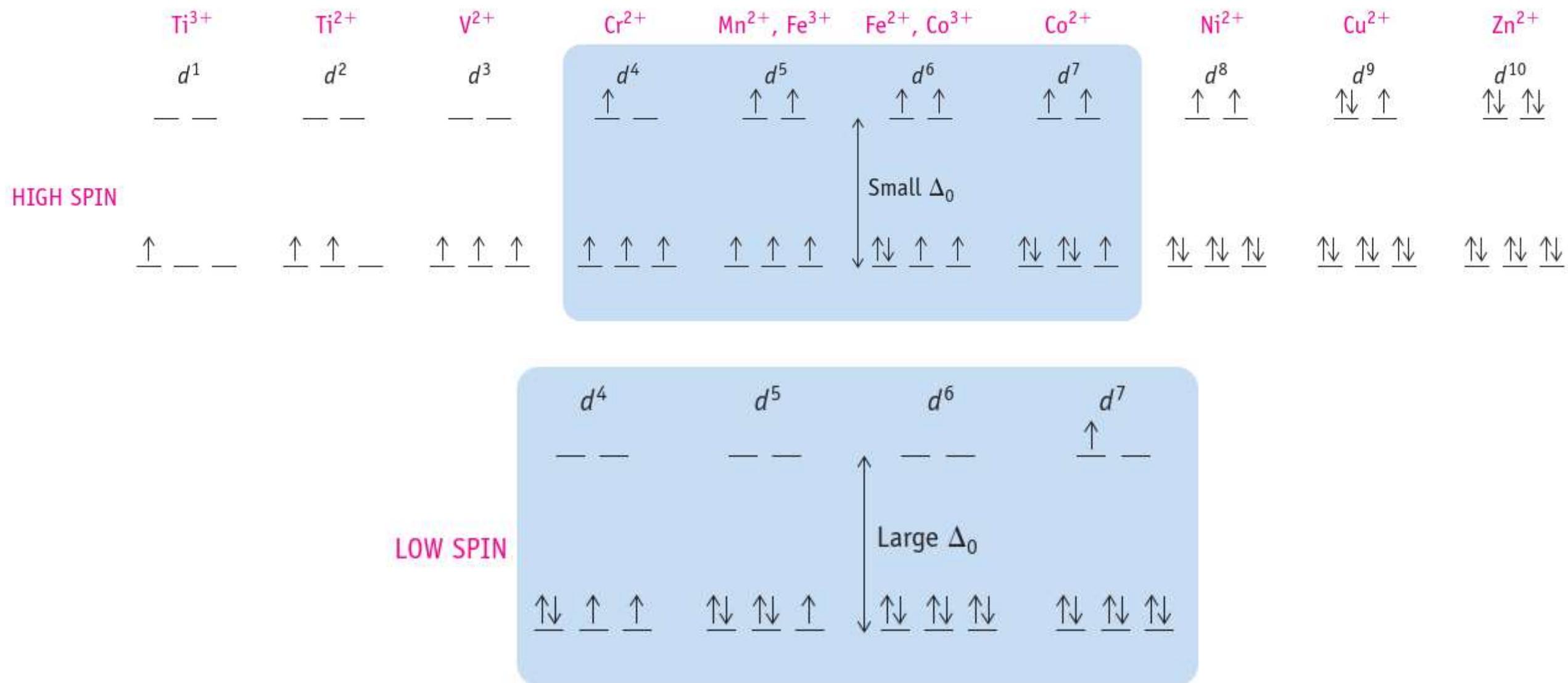


Figure 22.24 High- and low-spin octahedral complexes. d-Orbital occupancy for octahedral complexes of metal ions. Only the d⁴ through d⁷ cases have both high- and low-spin configurations.

❖ To determine whether a complex is high spin or low spin:

- Look at the **transition metal**.
 - ✓ First row metals will want to be high spin unless the ligand(s) force(s) it to be low spin.
 - ✓ Second row metals want to be low spin unless the ligand(s) forces it high spin.
 - ✓ Third row metals will be low spin.
 - Look at the **ligand(s)** as they will be the ultimate determining factor.
 - ✓ If the ligand matches the transition metal in terms of high spin/low spin, then the complex's spin will be whatever is "agreed" upon.
 - ✓ If they differ, ***follow the ligand's spin type***. If the ligand is classified *neither as high nor low spin*, follow the transition metal's spin type. Ligand spin types are enumerated below.
 - ✓ If there are *multiple ligands with differing spin types*, go with *whichever spin type is most abundant* in the complex.
- The ligands below are ranked ***from low spin*** (greatest energy difference between t_{2g} and e_g) to high spin (lowest energy difference):

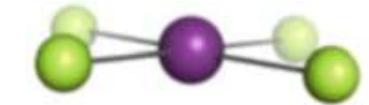


To illustrate this concept, let's take the following complexes: $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and $[\text{Ni}(\text{CN})_4]^{2-}$.

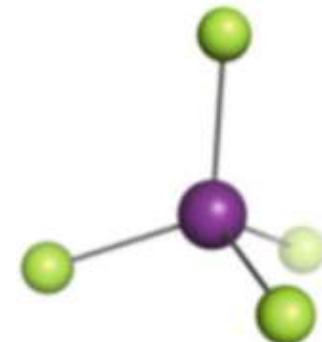
The nickel complexes all have the same oxidation state on the metal (2+), and thus the same d-electron count. In the first complex, nickel wants to be high spin, while ammonia prefers neither high nor low spin. Therefore, the complex will be high spin and emit blue light, which is an absorbance of orange—weak energy—light. For the second complex, nickel again wants to be high spin, but cyanide prefers low spin. As a result, the complex becomes low spin and will emit yellow light, which is an absorbance of violet—strong energy—light.

Tetrahedral and Square-planar configurations: 4-coordination complexes

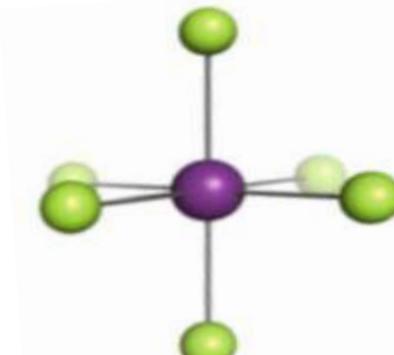
- Other than octahedral, two configurations that are common among the elements of the first transition series are the tetrahedral and square-planar configurations, both involving 4-coordination.
- The **square-planar configuration** may be considered as derived from the octahedral one by removing the ligands on the z-axis.
- An elongation of the M-L distances on the z-axis can lead to an **intermediate case** corresponds to elongation of the metal-ligand distances on the z-axis, to **unsymmetric substitution** on the z-axis in a complex such as MX_4Z_2 , (both of which are **tetragonal distortions**) or to the case of the 5-coordinated **square pyramidal configuration**.
- An elongation of the M-L distances on the z-axis leads to a decrease of the interaction between the ligand field and those metal orbitals with components in the z direction.



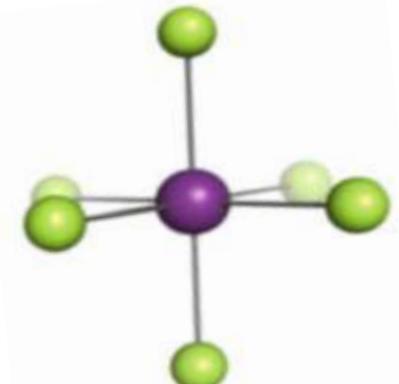
Square-planar



Tetrahedral



Octahedral



Z-axis elongated
Octahedral

□ Splitting of d-orbital energies in Tetrahedral complexes: Coordination number four

- Four-coordinate tetrahedral complexes are second only in abundance to octahedral complexes for the 3d metals.
- The same kind of arguments based on crystal-field theory can be applied to these species as we used for octahedral complexes.
- In the tetrahedral arrangement, no orbital points directly at a ligand in the tetrahedral case, but the d_{xy} , the d_{yz} , and the d_{zx} type lie closer to the ligand than $d_{x^2-y^2}$ or d_z^2 .
- Fig. 22.24 shows that the distances are as half the side of a cube compared with half the face diagonal. Consideration of the spatial arrangement of the orbitals shows that: the e orbitals ($d_{x^2-y^2}$ or d_z^2) point between the positions of the ligands and their partial negative charges, whereas the t_2 orbitals (d_{xy} , the d_{yz} , and the d_{zx}) point more directly towards the ligands.
- A tetrahedral crystal field **splits d orbitals into two sets** but with the **two e orbitals** (the $d_{x^2-y^2}$ and the d_z^2) **lower in energy** than the three t_2 orbitals (the d_{xy} , the d_{yz} , and the d_{zx}) (Fig. 20.8).
- Thus, **e orbitals lie below the t_2 orbitals.**

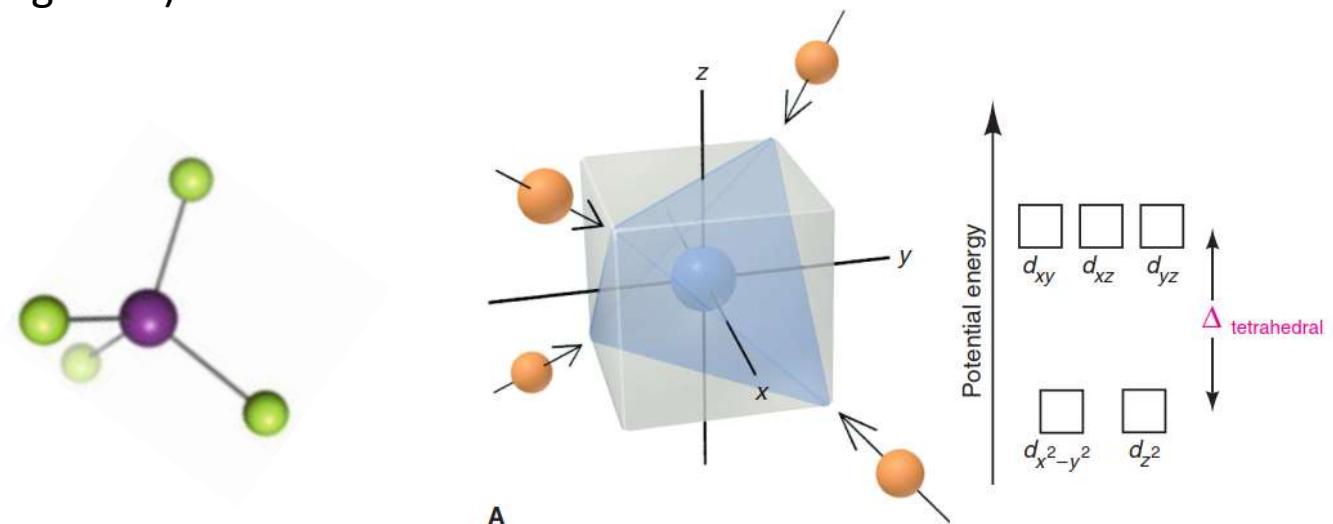


Figure 22.24 Splitting of d-orbital energies in 4 coordination tetrahedral complexes. The pattern of splitting by a **tetrahedral field of ligands** is the opposite of the octahedral pattern.

□ Splitting of d-orbital energies in Tetrahedral complexes: Coordination number four

Key points: In a tetrahedral complex, the e orbitals lie below the t_2 orbitals; only the *high-spin case* need be considered.

$$\Delta_T \approx \frac{4}{9} \Delta_O$$

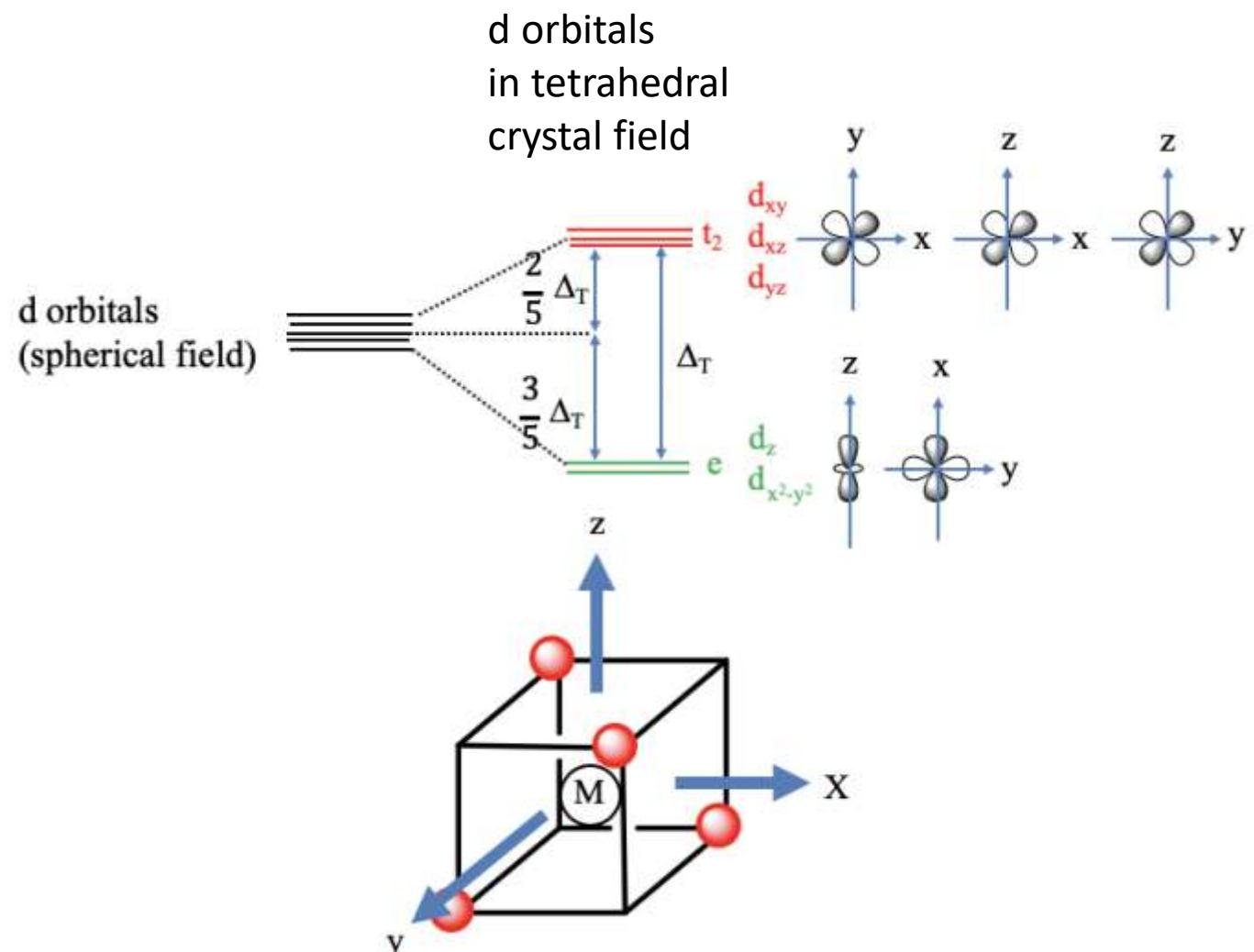


Figure 7.1.10 The orbital energy-level diagram used in the application of the building-up principle in a crystal-field analysis of a tetrahedral complex.

- In the point group T_d the $d_{x^2-y^2}$ or d_z^2 – orbitals are double-degenerate and have the symmetry type e. Because they are symmetrically degenerate, they are also energetically degenerate.
- The energy of the d_{xy} , the d_{yz} , and the d_{zx} orbitals have most of their energy density in between the axes. Therefore, their energies are increased relative to the spherical crystal field. They are increased by the same amount because the orbitals are triply degenerated in the point group T_d and have the symmetry type t_2 . *Because there is no center of inversion in a tetrahedral complex, the orbital designation does not include the parity label g or u.*
- The **energy difference** between the e and the t_2 orbitals is **called Δ_t** .
- The energy of the t_2 orbitals is decreased by $2/5 \Delta_t$. The energy of the e orbitals is increased by $3/5 \Delta_t$. This is again due to the law of the conservation of energy. The total amount of decreased energy must equal the total amount of increased energy.
- The **tetrahedral crystal field energy is smaller than that of the octahedral field (Δ_t is less than Δ_O)** because the octahedral field interacts more strongly with the d-orbitals compared to the tetrahedral field. One can calculate that it is actually just $4/9$ of the octahedral field ($\Delta_t \approx 4/9 \Delta_O$). This is mainly because the lobes of the t_2 orbitals do not point exactly toward the vertices of the tetrahedron, while the lobes of the e orbitals do point exactly toward the vertices of the octahedron. *The lack of direct interaction between orbitals and ligands in the tetrahedral configuration reduces the magnitude of the crystal field splitting by a geometrical factor equal to $2/3$, and the fact that there are only four ligands instead of six ($4/6$) reduces the ligand field by another $2/3$. The total splitting in the tetrahedral case is thus approximately $2/3 \times 2/3 = 4/9$ of the octahedral splitting.*
- ***The pairing energy is invariably more unfavorable than Δ_t , and normally only high-spin tetrahedral complexes are encountered.***
- In theory, alternative electron configurations are possible for the cases d^3 , d^4 , d^5 and d^6 in the tetrahedral field but the gain in CFSE (crystal field stabilization energy) is reduced by the smaller size of the splitting, and the loss of exchange energy is never counterbalanced. Thus, **all tetrahedral complexes are high spin**.

□ Tetragonally Distorted Octahedral and Square Planar Crystal Fields

- One nice feature of crystal field theory is that it can readily explain *distortions such as the tetragonal distortion* of octahedral complexes (Fig. 7.1.11).

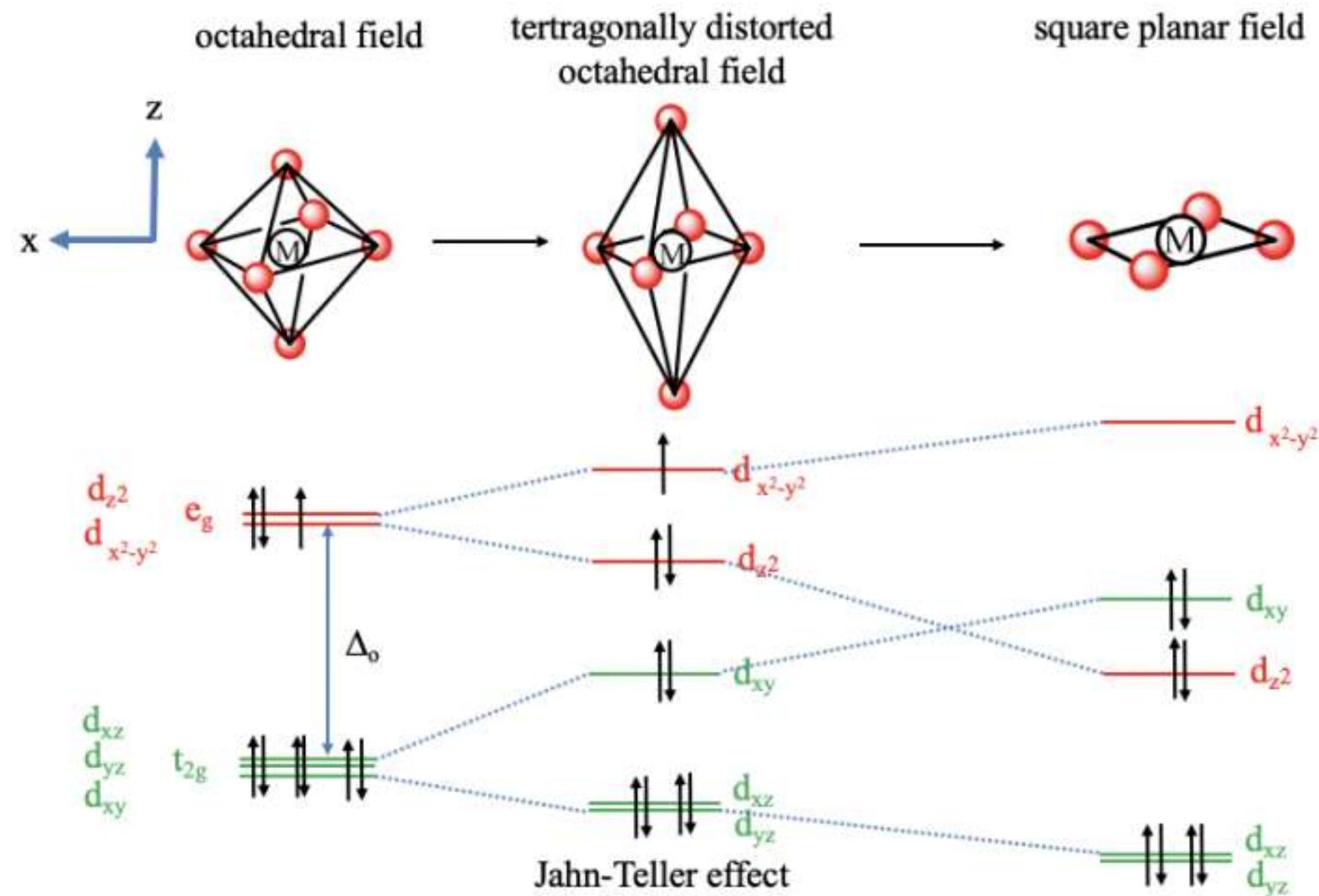


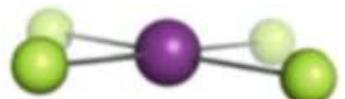
Figure 7.1.11 Tetragonal distortions in the octahedral crystal field leading to a square planar field.

- In a **tetragonally distorted complex there is a tetragonally distorted crystal field**.
- In an **elongated octahedron two ligands** are further away from the metal than the four others. Let us assume these two ligands are on the z-axis. Then, the crystal field is weaker on the z-axis. To keep the overall crystal field constant we must bring the other four ligands closer to the metal center. That means that we compress along the x and the y-axis. What will happen to the energy of the orbitals as the octahedron distorts? Because we elongate in the z-direction, the d_{z^2} orbital, that has most electron density on the z-axis goes down in energy. Because we compress on the x and the y-axis, the energy of the $d_{x^2-y^2}$ orbital increases.
- What about the t_{2g} orbitals? The d_{xy} orbital goes up in energy because it has electron density in the xy plane, but not along the z-axis. The d_{yz} and d_{zx} decrease in energy because they have a significant electron density in z-direction, and the electron density in z-direction is the same for both orbitals.
- We can now also think about, if the crystal field theory can explain why tetragonal distortion occurs preferentially for certain electron configurations of the metal. For example, it is known that metal ions with d^9 electron configuration often make octahedral complexes with tetragonal distortions. For instance, the hexaaqua copper (2+) complex is an example of a tetragonally distorted complex with a Cu^{2+} ion that has a d^9 electron configuration.
- We can understand that the tetragonal distortion occurs when comparing the energy of the electrons in the undistorted vs the distorted octahedron. In the undistorted octahedron we have three electrons in the degenerated e_g orbitals. As we distort, we can move two electrons in the energetically lower d_{z^2} -orbital and fill the third one into the energetically higher $d_{x^2-y^2}$ -orbital. Thus, overall the electrons have a lower energy explaining the distortion. This is an example of the **Jahn-Teller effect**.
- In general, ***the Jahn-Teller effect can occur when there are partially occupied degenerate orbitals***. In this case a molecule can lower its energy through distortion. Note that not only partial occupation of the e_g -orbitals, but also ***partial occupation of the t_{2g} -orbitals can cause the Jahn-Teller effect, although the effect is typically smaller***. For example in complexes with metal ions the d^4 -electron configuration, all four electrons can be stabilized through Jahn-Teller distortion. It should also be noted that in addition to an elongation, there is also the possibility of compressing the octahedron along the z-axis. In this case the order of energy of the d_{z^2} and the $d_{x^2-y^2}$ orbital reverses, and the order of energy of the d_{xy} , as well as the d_{yz} and d_{zx} reverses as well.

- Finally, let us look at the ***square planar crystal field in square planar complexes***.
- To understand the square planar crystal field it helps to understand the square planar shape as an infinitely elongated octahedron. If we move the two ligands along the z-axis infinitely far away from the metal ion, then we have created a square planar structure.
- How will the orbital energies change compared to an elongated octahedron?
- The $d_{x^2-y^2}$ orbital will have an even higher energy due to the necessity to compensate for the decreased field associated with the ligands on the z-axis by further compressing along the x and the y-axis. The d_{z^2} -orbital is even further decreased in energy because the ligands along the z-axis are now completely gone. The d_{xy} orbital is increased in energy because of the enhanced field in the xy-plane. It is now higher than the d_{z^2} -orbital. The d_{yz} and the d_{zx} orbitals are further decreased in energy because they have significant electron density in z-direction.
- Viewing the square planar shape as an extreme case of a tetragonally elongated octahedron also lets us understand why the square planar shape is so often adopted by d⁸-metal complexes.
- We can see that the stabilization energy, and thus the tendency to distort is the greatest when two electrons are in the metal e_g orbitals. In this case two electrons lower their energy through distortion and no electron has an increased energy. Thus, we would understand that the distortion becomes so great, so that the octahedral complex eventually loses two ligands and adopts the square planar shape. This is a nice example how crystal field theory can explain shapes and the number of bonds in a complex without actually being a bonding theory.

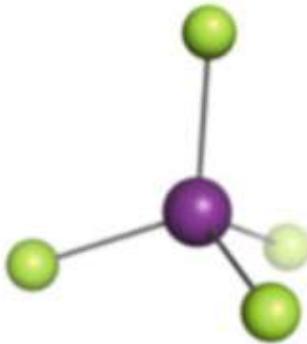
Coordination number four: Square Planar Complex

➤ Which of the following geometries is the **less sterically demanding arrangement?**

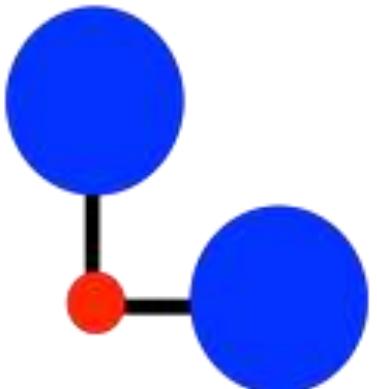


Square-planar

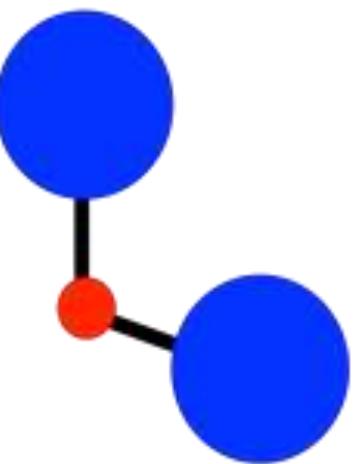
vs.



Tetrahedral



square planar
 90°



tetrahedral
 109°

- In a tetrahedron, all the ligands are 109.5° from each other.
- In a square planar geometry, the ligands are only 90° from each other.
- Tetrahedral geometry is always less crowded than square planar, so that factor always provides a bias toward tetrahedral geometry.
- As a result, we might expect *square planar geometry to occur only when steric is heavily outweighed by ligand field stabilization energy.*

- Complexes with four ligands in a plane containing the central metal are termed square planar complexes.
- It is easier to understand the electronic energy levels of the d orbitals in square planar complexes by starting from those for hexacoordinate octahedral complexes.
- Placing the six ligands along the Cartesian axes, the two ligands on the z-axis are gradually removed from the central metal, and finally, only four ligands are left on the xy plane.
- The interaction of the two z-coordinate ligands with the d_{z^2} , d_{xz} , and d_{yz} orbitals becomes smaller, and the energy levels of these ligands lower.
- On the other hand, the remaining four ligands approach the metal, and the $d_{x^2-y^2}$ and d_{xy} energy levels rise as a result of the removal of the two ligands.
- This results in the order of the energy levels of five d orbitals being d_{xz} , $d_{yz} < d_{z^2} < d_{xy} \ll d_{x^2-y^2}$ (Figure 6.2.7).
- Rh⁺, Ir⁺, Pd²⁺, Pt²⁺, and Au³⁺ complexes with a d⁸ configuration tend to form square planar structures because eight electrons occupy the lower orbitals leaving the highest $d_{x^2-y^2}$ orbital empty.

- The energy levels therefore split as indicated in Fig. 13.8a with the d_{z^2} level and the d_{xz} and d_{yz} levels falling below the others.
- The $d_{x^2-y^2}$ and d_{xy} levels rise slightly as the metal-ligand distances in the xy plane shorten a little because of the decrease in repulsion from the z ligands.
- If the z ligands are removed completely to give the ***square-planar configuration***, the energy level diagram of Fig. 13.8b results. Here, the d_{z^2} and d_{xy} levels have crossed over. Notice that, ***as the configuration in the xy plane is similar to that in the octahedron***, the energy separation between $d_{x^2-y^2}$ and d_{xy} remains practically the same as the ***octahedral Δ_o*** .

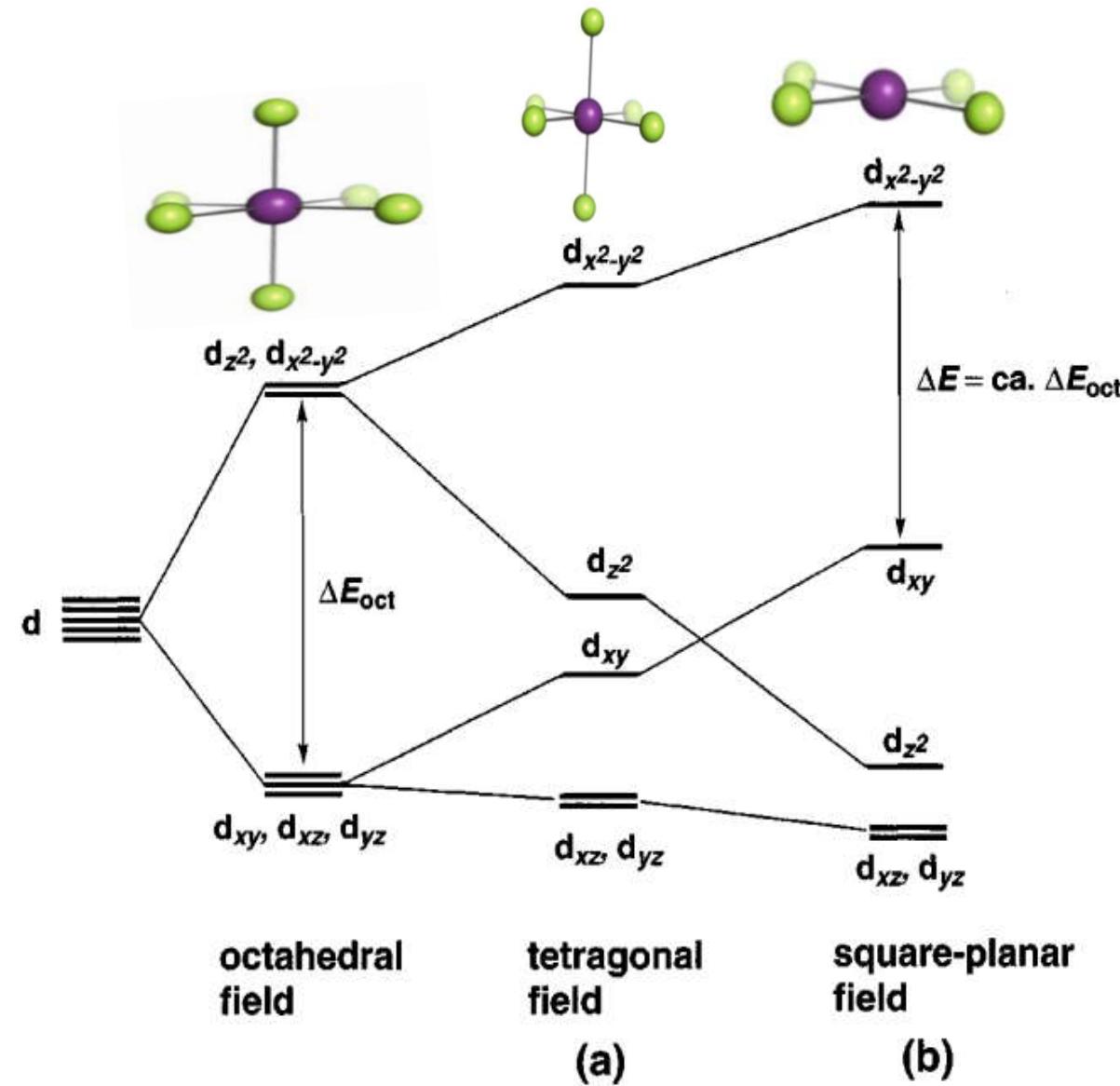


FIG. 13.8 Effect on orbital energies of removing ligands on the z axis, starting from an octahedron:
 (a) the tetragonal field with nonequivalent z ligands, (b) the square-planar field with no z ligands

□ Square-planar complexes : Coordination number four

- Although a *tetrahedral arrangement of four ligands is the least sterically demanding arrangement, some complexes exist with four ligands in an apparently higher-energy square-planar arrangement.*
- If only electrostatic interactions are considered, a square-planar arrangement of ligands gives the d-orbital splitting shown in Fig. 20.10 , with $d_{x^2-y^2}$ raised above all the others.
- This arrangement may become **energetically favorable when there are eight d electrons, and the crystal field is strong enough to favor the low-spin $d_{yz}^2 d_{zx}^2 d_{z^2}^2 d_{xy}^2$ configuration.**
- **In this configuration the electronic stabilization energy can more than compensate for any unfavorable steric interactions.**

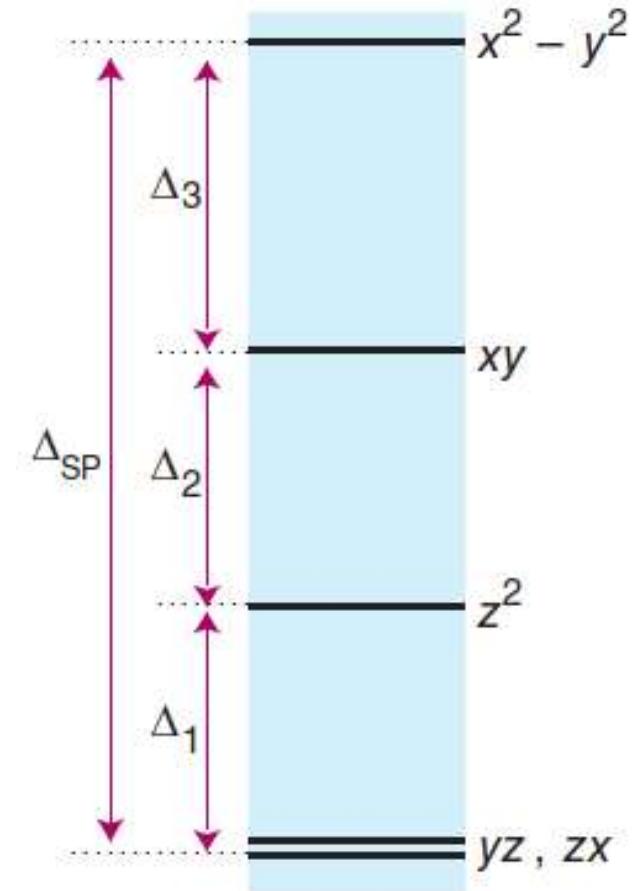


Figure 20.10 The orbital splitting parameters for a square-planar complex.

Square-planar complexes : Coordination number four

Key points: A d^8 configuration, *coupled with a strong crystal field*, favors the formation of square-planar complexes.

- *This tendency is enhanced with the 4d and 5d metals because of their larger size and the greater ease of electron pairing.*
- Thus, many square-planar complexes are found for complexes of the **large** $4d^8$ and $5d^8$ Rh(I), Ir(I), Pt(II), Pd(II), and Au(III) ions, in which *unfavorable steric constraints have less effect, and there is a large ligand-field splitting associated with the 4d- and 5d-series metals.*
- One should note that **pairing energies** for the 4d- and 5d-series metals *tend to be lower* than for the 3d-series metals, and *this difference provides a further factor* that favors the formation of low-spin square-planar complexes with these metals.

- The d⁸ metal ions, such as [PdCl₄]²⁻, form square planar complex.
- By contrast, small 3d-series metal complexes such as [NiX₄]²⁻, with X a halide, are *generally tetrahedral* because the ligand-field splitting parameter is generally quite small and *will not compensate sufficiently for the unfavorable steric interactions*.
- However, only *when the ligand is high in the spectrochemical series is the CFSE large enough to result in the formation of a square-planar complex*, as, for example, with [Ni(CN)₄]²⁻.
- In the *square planar case, only low-spin complexes* have been found.
- *Square-planar complexes are low spin and usually diamagnetic* because the four pairs of d electrons fill the four lowest-energy orbitals.

□ Calculation of Crystal (Ligand)-field stabilization energies (CFSE or LFSE)

Definition: Crystal Field Stabilization Energy (CFSE)

- The crystal field stabilization energy is defined as the energy of the electron configuration in the crystal field minus the energy of the electronic configuration in the spherical field.

$$\text{CFSE} = \Delta E = E_{\text{crystal field}} - E_{\text{spherical field}}$$

- The CSFE will depend on multiple factors including:
- Geometry (crystal field splitting pattern)
 - Number of d-electrons
 - Spin Pairing Energy (the contribution of spin pairing energy is often negligible in comparison to other contributions and is omitted at times)

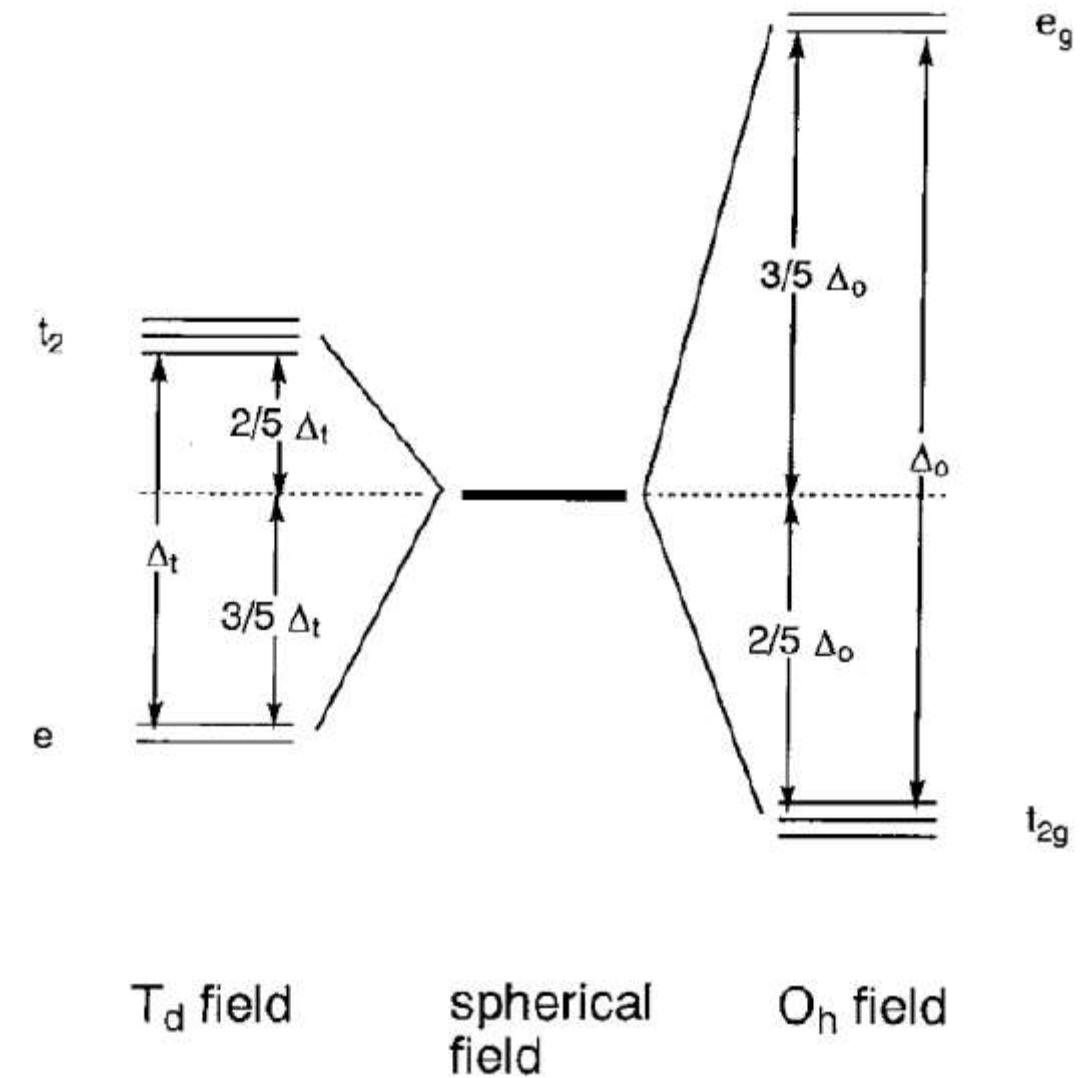


Figure 6.2.6: Ligand field splitting in tetrahedral and octahedral complexes.

- For an octahedral complex, each of the more stable t_{2g} orbitals are stabilized by $-0.4\Delta_o$ relative to spherical field whereas the higher energy e_g orbitals are destabilized by $+0.6\Delta_o$. For a complex the stabilization or destabilization of each electron is summed. Any electrons that are paired within a single orbital, also contribute spin pairing energy ($+P$). The overall CFSE for a complex is expressed as a multiple of the crystal field splitting parameter Δ_o .
- If the energy difference between the t_{2g} and e_g levels is defined as Δ_o or $10 Dq$, then the e_g set will be raised by $0.6\Delta_o$ ($6 Dq$) and the t_{2g} set will be lowered by $0.4\Delta_o$ ($4 Dq$) relative to the barycenter.
- Thus, six of the electrons in the d^{10} electron configuration would be stabilized by $4Dq$ each (for a total stabilization of $24Dq$) and the other four electrons would be destabilized by $6Dq$ each (for a total destabilization of $24 Dq$). Overall, the energy of the 10 electrons occupying the d -orbitals in an octahedral CF would be identical to that of the barycenter.
- It is this splitting of the d -orbitals by the CF that causes the coordination compounds to be colored. If the light of the appropriate wavelength is shone on the molecule, an electron from the lower lying t_{2g} set can be photochemically excited to an empty orbital in the e_g set, causing an electronic absorption in the visible region.

- Transition metal ions have 0 to 10 d electrons and when the split d orbitals are filled from a lower energy level, the electron configuration $t_{2g}^x e_g^y$ corresponding to each ion is obtained.
- With the zero energy level chosen as the average energy level, the energy of the electron configuration relative to zero energy becomes
 - $\text{CFSE} (= \text{LFSE}) = (-0.4x + 0.6y)\Delta_0$
- This value is called the **crystal field stabilization energy (CFSE) (or ligand field stabilization energy (LFSE))**.
- The electron configuration with a smaller value (taking the minus sign into consideration) is more stable.
- LFSE is an important parameter to explain some properties of d-block transition metal complexes.

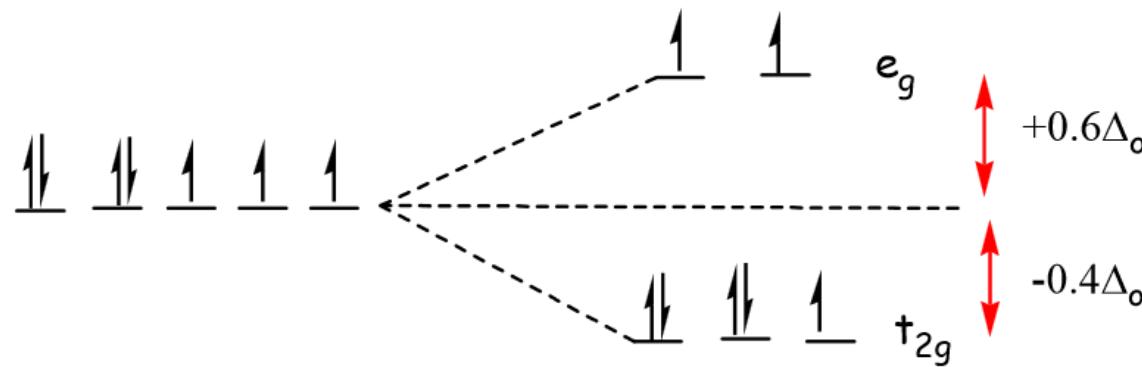
- A condition other than the orbital energy level is required to explain the filling of electrons being populated into the split t_{2g} and e_g orbitals.
- Two electrons can occupy an orbital with anti-parallel spins but a strong electrostatic repulsion occurs between two electrons in the same orbital. This repulsive interaction is called **pairing energy, P** (which **varies between 200–400 kJmol⁻¹** depending on the metal.).
- When the number of d electrons is less than three, the pairing energy is minimized by loading the electrons in the t_{2g} orbital with parallel spins. Namely, the electron configurations arising are t_{2g}^1 , t_{2g}^2 , or t_{2g}^3 .
- Two possibilities arise when the fourth electron occupies either of the t_{2g} or e_g orbitals. The lower energy orbital t_{2g} is favorable but occupation of the same orbital gives rise to **pairing energy, P** . The total energy becomes
- $-0.4\Delta_o \times 4 + P = -1.6\Delta_o + P$
- If the fourth electron occupies the energetically unfavorable e_g orbital, the total energy becomes
- $-0.4\Delta_o \times 3 + 0.6\Delta_o = -0.6\Delta_o$

- The choice of the electron configuration depends on which of the above values is larger. Therefore, if $\Delta_o > P$, t_{2g}^4 is favored and this is called the strong field case or the **low spin** electron configuration.
- If $\Delta_o < P$, $t_{2g}^3e_g^1$ is favored and this is called the weak field case or the **high spin** electron configuration.
- A similar choice is required for d⁵, d⁶, and d⁷ octahedral complexes, and in the strong field case, t_{2g}^5 , t_{2g}^6 , or $t_{2g}^6e_g^1$ configurations are favored, whereas, in the weak field case, $t_{2g}^3e_g^2$, $t_{2g}^4e_g^2$, or $t_{2g}^5e_g^2$ configurations are favored.
- The ligand field splitting parameter Δ_o is decided by the nature of the ligands and metal, whereas *the pairing energy, P, is almost constant* and shows only a slight dependence on the identity of the metal.

❖ What is the CFSE for a high spin d₇ octahedral complex?

Solution

The splitting pattern and electron configuration for both spherical and octahedral ligand fields are compared below.



The energy of the spherical field ($E_{\text{spherical field}}$) is: $E_{\text{spherical field}} = 7 \times 0 + 2P = 2P$.

The energy of the octahedral crystal field $E_{\text{oct field}}$ is: $E_{\text{oct field}} = (5 \times -0.4\Delta_o) + (2 \times 0.6\Delta_o) + 2P = -0.8\Delta_o + 2P$.

So, the CFSE is: $\text{CFSE} = E_{\text{oct field}} - E_{\text{spherical field}} = (-0.8\Delta_o + 2P) - 2P = -0.8\Delta_o$

Notice that **the spin pairing energy cancels out in this case** (and **will when calculating the CFSE of high spin complexes**) since the number of paired electrons in the octahedral field is the same as that in spherical field of the free metal ion.

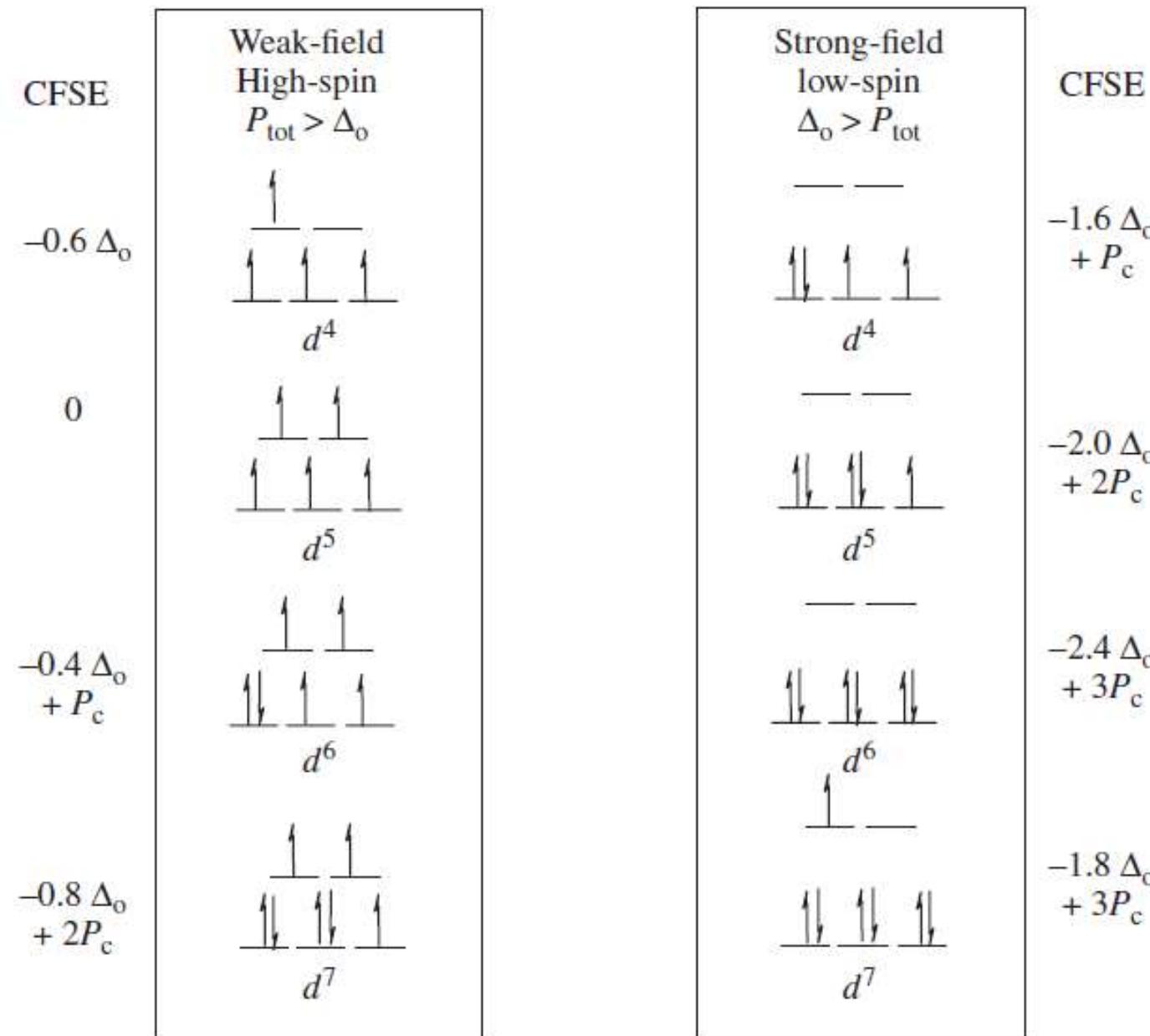
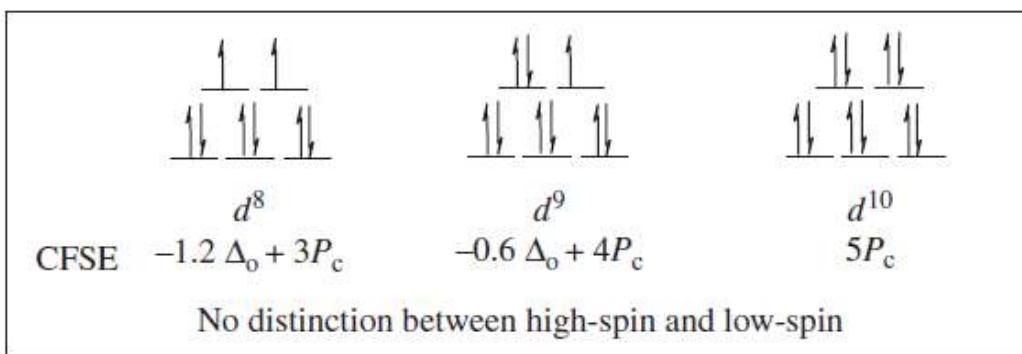
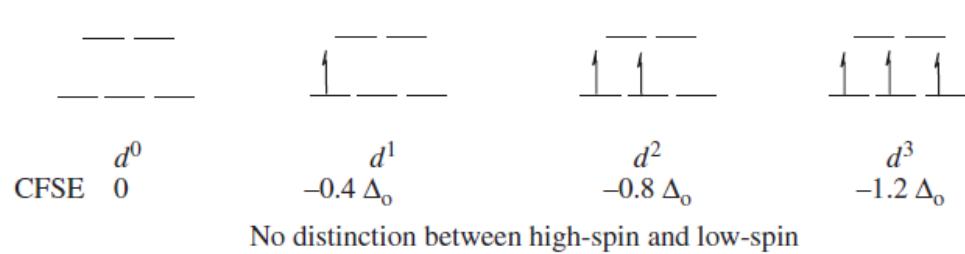


FIGURE 16.9
Crystal field splitting diagram for the different d^n configurations in an octahedral CF and their crystal field splitting energy. P_c = Coulomb pairing energies.

- Ligand-field stabilization energies can be calculated in the same way as for octahedral complexes. Since tetrahedral complexes are always high-spin, there is never any need to consider the *pairing energy* in the LFSE, and the only differences compared with octahedral complexes are the order of occupation (e before t_2) and the contribution of each orbital to the total energy ($- \frac{3}{5} \Delta_T$ for an electron in e orbital and $+ \frac{2}{5} \Delta_T$ for a t_2 orbital).
- The CFSE values for these high-spin configurations are given in Table 9.2.1.
- It will be seen that *the CFSE in an octahedral configuration is always greater than that in the corresponding tetrahedral configuration, except in the cases of d^0 , d^5 and d^{10}* where both values are zero.
- The configurations with the next smallest CFSE loss in the tetrahedral field compared to the octahedral field are d^1 and d^6 if the octahedral state is high spin.
- *The adoption of 4-coordination rather than 6-coordination is expected, in general, to be accompanied by loss of energy of formation* as only four interactions occur instead of six.
- In addition, *there is commonly a loss of CFSE as well*.

Table 9.2.1: Crystal field stabilization energies (CFSE) for high and low spin octahedral complexes

	Total d-electrons	Spherical Field		Octahedral Field		Crystal Field Stabilization Energy		
				High Spin		Low Spin		
		$E_{\text{spherical field}}$	Configuration	$E_{\text{crystal field}}$	Configuration	$E_{\text{crystal field}}$	High Spin	Low Spin
Example	d ⁰	0	$t_{2g}^0 e_g^0$	0	$t_{2g}^0 e_g^0$	0	0	0
Ti ³⁺	d ¹	0	$t_{2g}^1 e_g^0$	-2/5 Δ_o	$t_{2g}^1 e_g^0$	-2/5 Δ_o	-2/5 Δ_o	-2/5 Δ_o
V ³⁺	d ²	0	$t_{2g}^2 e_g^0$	-4/5 Δ_o	$t_{2g}^2 e_g^0$	-4/5 Δ_o	-4/5 Δ_o	-4/5 Δ_o
Cr ^{3+, V²⁺}	d ³	0	$t_{2g}^3 e_g^0$	-6/5 Δ_o	$t_{2g}^3 e_g^0$	-6/5 Δ_o	-6/5 Δ_o	-6/5 Δ_o
Cr ^{2+, Mn³⁺}	d ⁴	0	$t_{2g}^3 e_g^1$	-3/5 Δ_o	$t_{2g}^4 e_g^0$	-8/5 $\Delta_o + P$	-3/5 Δ_o	-8/5 $\Delta_o + P$
Mn ^{2+, Fe³⁺}	d ⁵	0	$t_{2g}^3 e_g^2$	0 Δ_o	$t_{2g}^5 e_g^0$	-10/5 $\Delta_o + 2P$	0 Δ_o	-10/5 $\Delta_o + 2P$
Fe ^{2+, Co³⁺}	d ⁶	P	$t_{2g}^4 e_g^2$	-2/5 $\Delta_o + P$	$t_{2g}^6 e_g^0$	-12/5 $\Delta_o + 3P$	-2/5 Δ_o	-12/5 $\Delta_o + P$
Co ²⁺	d ⁷	2P	$t_{2g}^5 e_g^2$	-4/5 $\Delta_o + 2P$	$t_{2g}^6 e_g^1$	-9/5 $\Delta_o + 3P$	-4/5 Δ_o	-9/5 $\Delta_o + P$
Ni ²⁺	d ⁸	3P	$t_{2g}^6 e_g^2$	-6/5 $\Delta_o + 3P$	$t_{2g}^6 e_g^2$	-6/5 $\Delta_o + 3P$	-6/5 Δ_o	-6/5 Δ_o
Cu ²⁺	d ⁹	4P	$t_{2g}^6 e_g^3$	-3/5 $\Delta_o + 4P$	$t_{2g}^6 e_g^3$	-3/5 $\Delta_o + 4P$	-3/5 Δ_o	-3/5 Δ_o
Cu ¹⁺	d ¹⁰	5P	$t_{2g}^6 e_g^4$	0 $\Delta_o + 5P$	$t_{2g}^6 e_g^4$	0 $\Delta_o + 5P$	0	0

Table 20.4 lists the configurations of tetrahedral d^n complexes together with the calculated values of the LFSE, and Table 20.5 lists some experimental values of Δ_T for a number of complexes.

Table 20.4 Ligand-field stabilization energies for tetrahedral complexes*

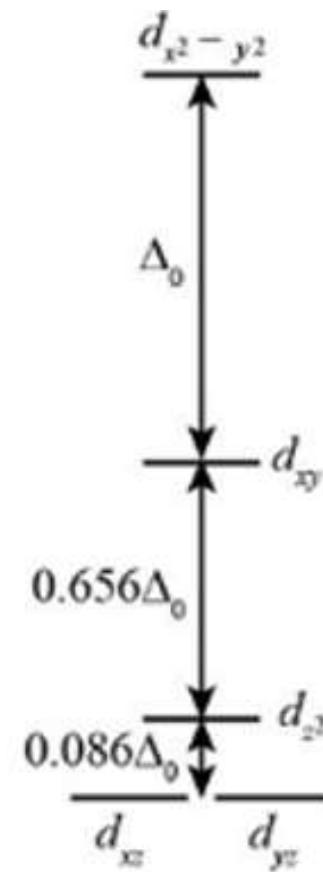
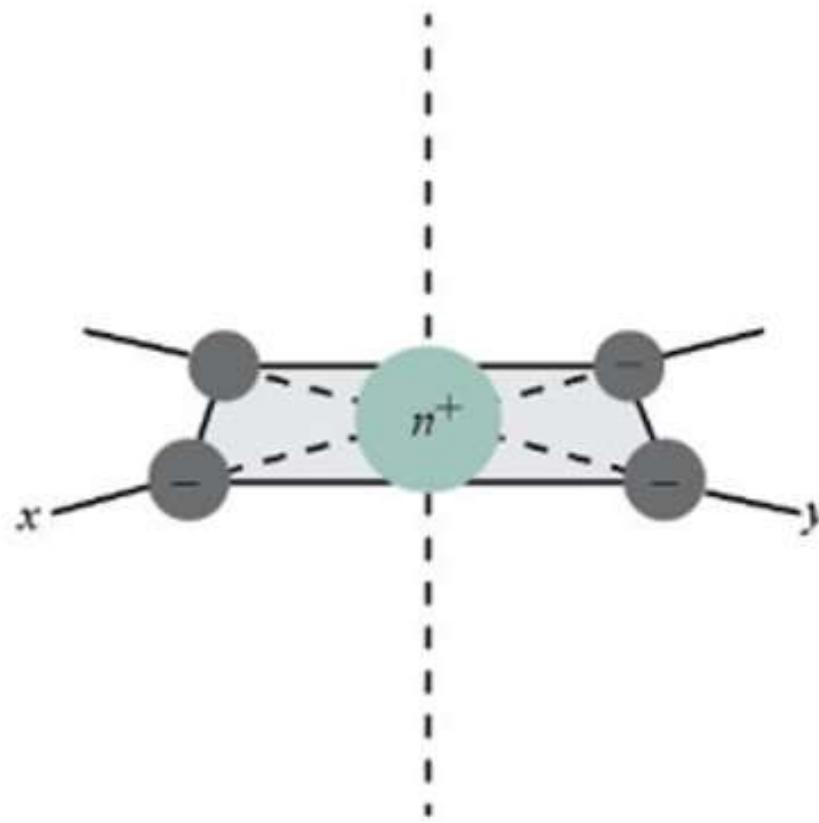
d^n	Config.	N	LFSE/ Δ_T
d^0		0	0
d^1	e^1	1	-0.6
d^2	e^2	2	-1.2
d^3	$e^2t_2^1$	3	-0.8
d^4	$e^2t_2^2$	4	-0.4
d^5	$e^2t_2^3$	5	0
d^6	$e^3t_2^3$	4	-0.6
d^7	$e^4t_2^3$	3	-1.2
d^8	$e^4t_2^4$	2	-0.8
d^9	$e^4t_2^5$	1	-0.4
d^{10}	$e^4t_2^6$	0	0

* N is the number of unpaired electrons.

Table 20.5 Values of Δ_T for representative tetrahedral complexes

Complex	Δ_T/cm^{-1}
$[\text{VCl}_4]$	9010
$[\text{CoCl}_4]^{2-}$	3300
$[\text{CoBr}_4]^{2-}$	2900
$[\text{CoI}_4]^{2-}$	2700
$[\text{Co}(\text{NCS})_4]^{2-}$	4700

□ Calculation of Crystal (Ligand)-field stabilization energies (CFSE or LFSE)



Splitting of the degenerate d-orbitals due to a square planar ligand field

Octahedral vs. tetrahedral (vs. square planar) coordination

Key points: Consideration of the CFSE (LFSE) predicts that

- ✓ **d³ and d⁸ ions strongly prefer an octahedral geometry over a tetrahedral one;**
- ✓ *for other configurations the preference is less pronounced;*
- ✓ *CFSE has no bearing on the geometry of d⁰, high-spin d⁵, and d¹⁰ ions.*
- An octahedral complex has six M–L bonding interactions and, *in the absence of significant steric and electronic effects*, this arrangement will have a lower energy than a tetrahedral complex with just four M–L bonding interactions.
- We can now complete the discussion by considering the electronic effects that favor an octahedral complex over a tetrahedral one.
- These considerations, and the data for the CFSE values, allow a prediction of the most probable cases in which 4-coordination will be found for transition elements of the first series.
- The geometry of complexes of ions with d⁰, d⁵, and d¹⁰ configurations will not be affected by the number of *d* electrons, as there is no LFSE for these species.

Definition: Octahedral Site Preference Energies (OSPE)

- The octahedral site preference energy (OSPE) is defined as the difference of CFSE energies for a non-octahedral complex and the octahedral complex. For comparing the preference of forming an octahedral ligand field vs. a tetrahedral ligand field, the OSPE is thus:

$$\text{OSPE} = \text{CFSE}(\text{oct}) - \text{CFSE}(\text{tet})$$

- From a simple inspection of Figure 9.2.1, the following observations can be made:
 - The OSPE is small in d^1 , d^2 , d^5 , d^6 , d^7 high spin complexes and other factors influence the stability of the complexes including steric factors.
 - The ***OSPE is large in d^3 and d^8 high spin complexes which strongly favor octahedral geometries.***
- The "***double-humped***" curve in Figure 9.2.1 is found for various properties of the first-row transition metals, including hydration and lattice energies of the M(II) ions, ionic radii as well as the stability of M(II) complexes. ***This suggests that these properties are somehow related to crystal field effects.***

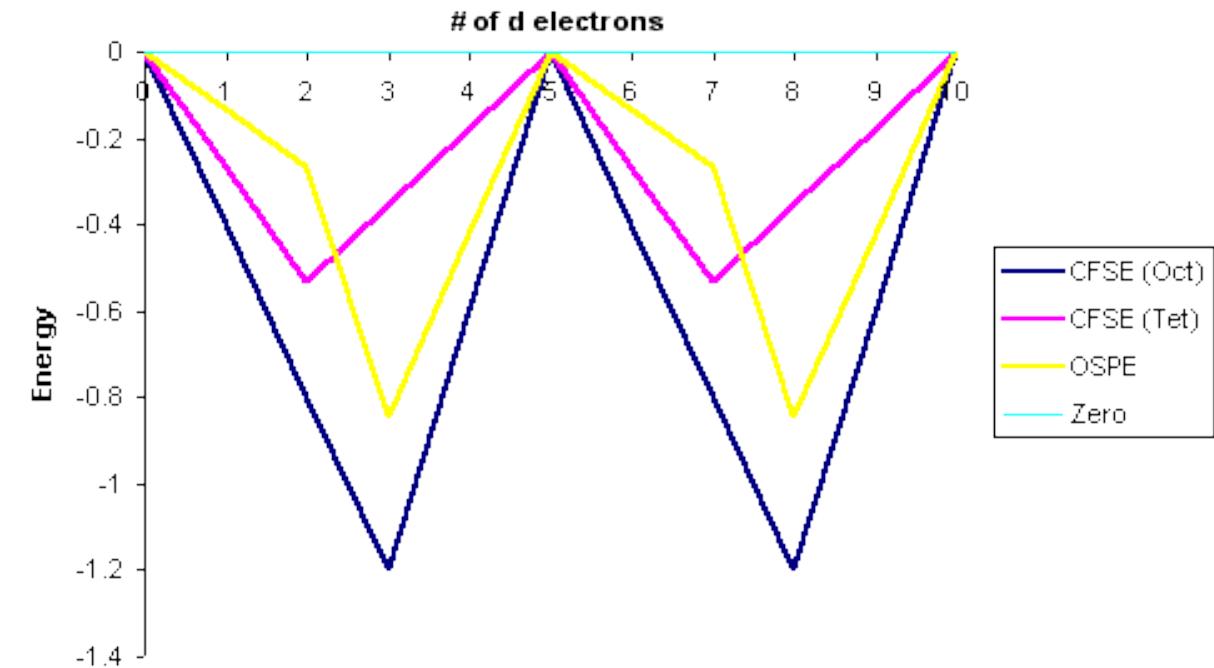


Figure 9.2.1: Crystal Field Stabilization Energies for both high spin octahedral fields (CFSE_{oct}) and tetrahedral fields (CFSE_{tet}). Octahedral Site Preference Energies (OSPE) are in yellow. This is for high spin complexes only.

- Figure 20.13 illustrates the variation of the LFSE (CFSE) for tetrahedral and high-spin octahedral complexes for all electronic configurations.
- It is apparent that, in terms of LFSE, ***octahedral geometries are strongly preferred over tetrahedral for d^3 and d^8 complexes***: chromium(III) (d^3) and nickel(II) (d^8) do indeed show an exceptional preference for octahedral geometries.
- *Similarly, d^4 and d^9 configurations show a preference for octahedral complexes (for example Mn(III) and Cu(II); note that the Jahn–Teller effect enhances this preference),*
- ✓ whereas *tetrahedral complexes of d^1 , d^2 , d^6 , and d^7 ions will not be too disfavored*; thus V(II) (d^2) and Co(II) (d^7) form tetrahedral complexes ($[MX_4]^{2-}$) with chloride, bromide, and iodide ligands.

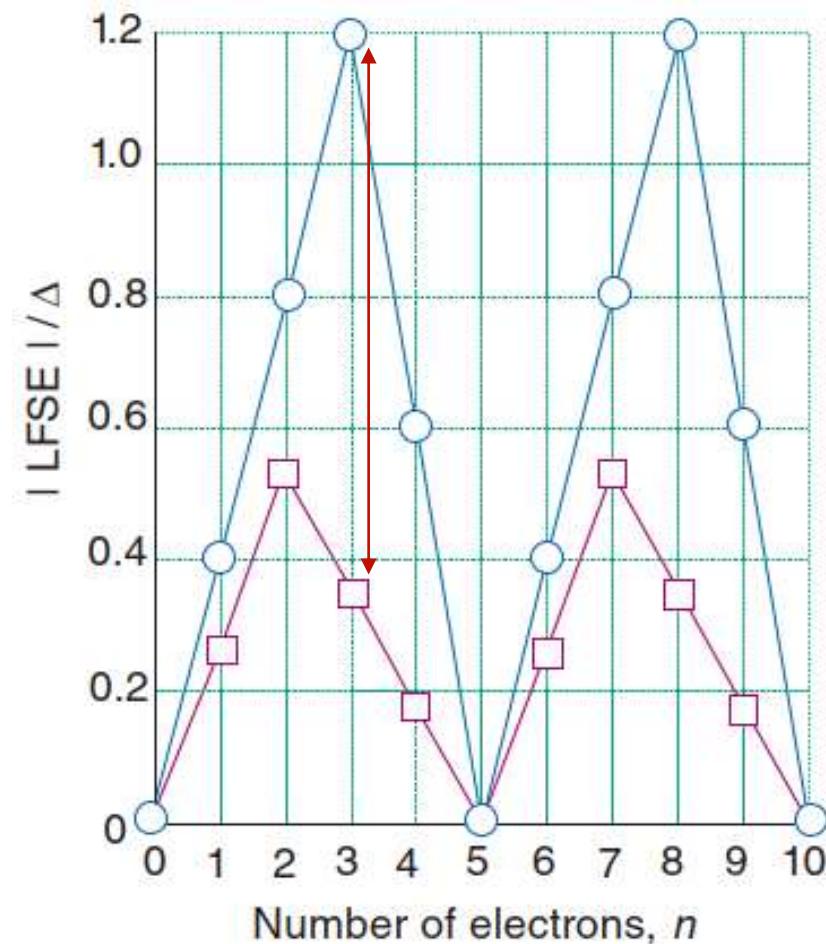


Figure 20.13 The ligand-field stabilization energy for d^n complexes in octahedral (high-spin, circles) and tetrahedral (squares) complexes. The LFSE is shown in terms of Δ_0 , by applying the relation $\Delta_T = \frac{4}{9} \Delta_0$.

- The tetrahedral configuration is expected to be unfavorable compared with the octahedral one, *except in the case of large ligands with low positions in the spectrochemical series, or in the ions with 0, (1), 5, (6) or 10 d electrons.*
- The **larger ligands** will experience steric hindrance to formation of 6-coordinated complexes and the interactions will also be reduced due to the increased metal-ligand distances.
- The **low position in the spectrochemical series** ensures that any loss of CFSE is not too serious due to the low intrinsic value of ΔE (similarly, *a low charge on the transition metal ion affects the ΔE value so divalent ions should form tetrahedral complexes more readily than trivalent ones, and a fortiori for lower charges*).
- Finally, the d configurations listed are those with the lowest CFSE differences. In practice, *tetrahedral complexes are typically formed by the halides (except fluoride) and related ligands.*

- The case of the square-planar configuration is rather different. Because the bond distances in the xy plane are essentially the same in octahedral and square-planar configurations, steric effects are negligible and the increase in attractions due to *forming six bonds rather than four will normally overwhelmingly favor* the regular octahedral complex.
- ***Changes in CFSE for low numbers of d electrons either favor the octahedral case or are small.*** Consider, however, the case of d^8 . In an octahedral complex, there are two electrons in the e_g level, while the square-planar configuration allows these to be paired in the d_{xy} orbital (Fig. 13.10) with a gain in CFSE of about $2\Delta E_{\text{oct}}$. (*This is only approximate* as the lower levels in the square-planar case do not match the octahedral t_{2g} levels, but they are quite close.)
- This is offset by a reduction in exchange energy from the 13K of the octahedral case to 12K for two sets of four electrons. However, ***if ΔE is sufficiently large, it is possible for the gain in CFSE to overbalance the loss in bonding interactions and the small loss in exchange energy.***
- It is found that *square-planar complexes are indeed formed by d^8 ions with ligands to the right of the spectrochemical series*: for example, Ni^{2+} forms a square-planar cyanide complex, $\text{Ni}(\text{CN})_4^{2-}$, while its hydrate or ammine are octahedral, e.g., $\text{Ni}(\text{NH}_3)_6^{2+}$. The larger ΔE values of heavier elements or of more highly charged elements extend the scope of formation of square complexes. Thus, all complexes, even halides, of platinum (II) and gold (III) (both d^8) are square-planar.

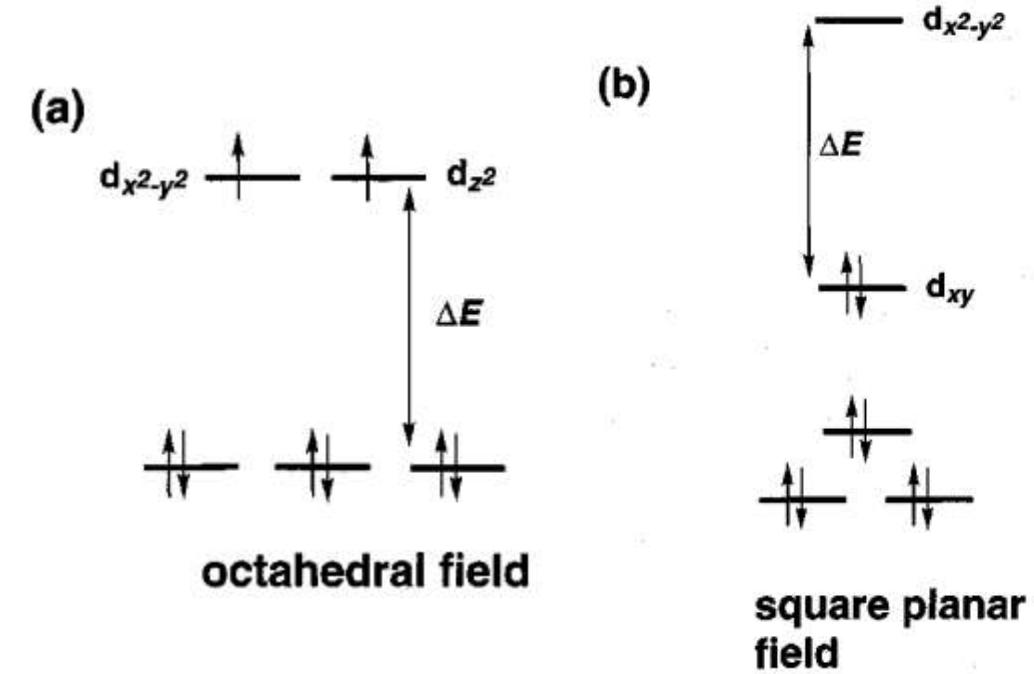


FIG. 13.10 The configuration of electrons in a d complex: (a) octahedral and (b) square-planar.

- Steric interactions favor a tetrahedral geometry for four-coordinate compounds (as per valence-shell electron-pair repulsion (VSEPR) theory), but ***square planar geometry can occur for electronic reasons***, which happens most often with a LS d⁸ electron configuration.
- The reason for this is because there is such a large separation between the b_{1g} and b_{2g} MOs. If the complex is LS d⁸, it will have an **extremely favorable CFSE of $-24.56\Delta_0$** . Thus, square planar compounds are often always LS.

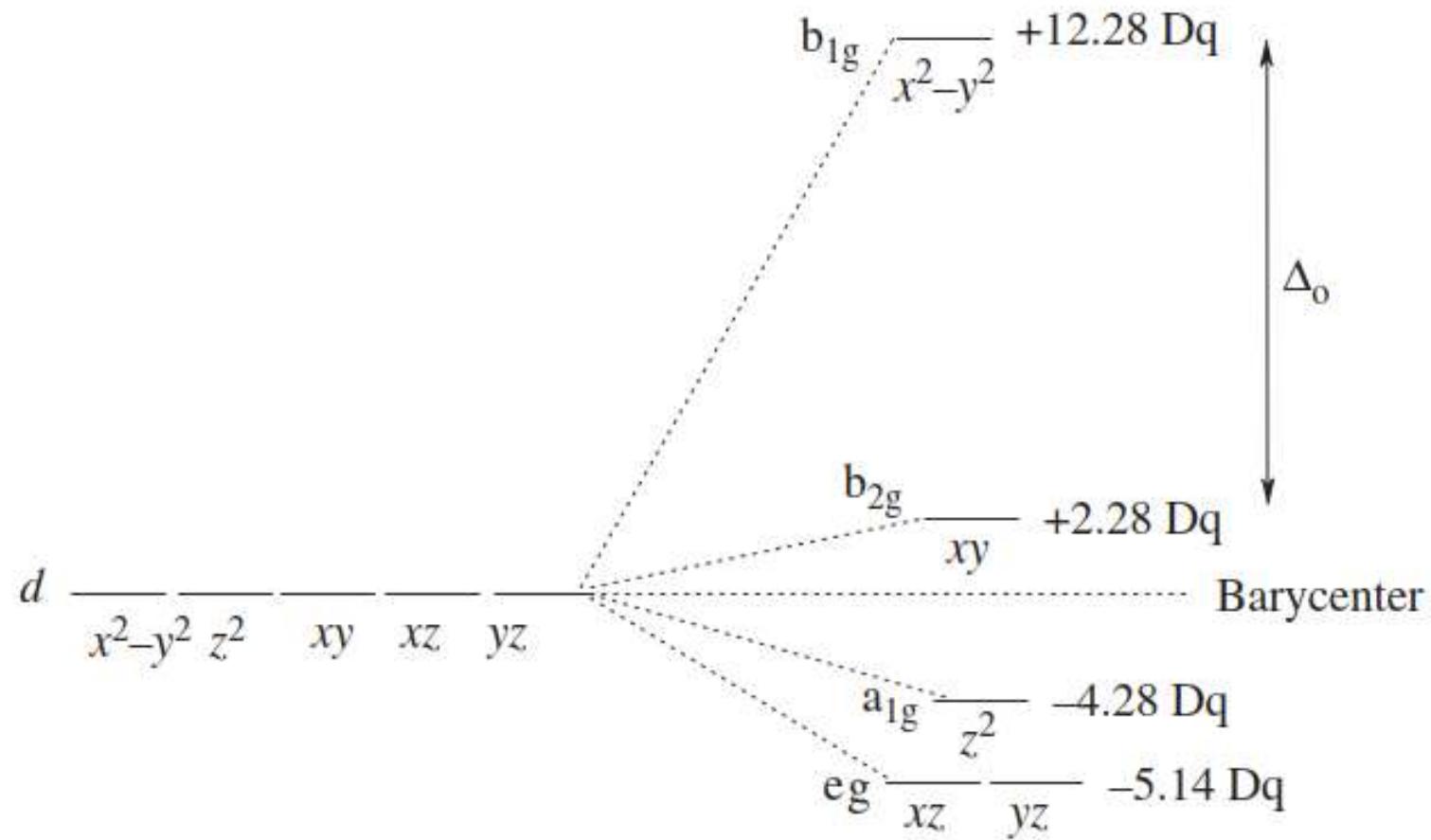


FIGURE 16.15 Crystal field splitting pattern for the **square planar geometry**.

- This extra CFSE found in square-planar complexes of d⁸ elements also occurs for the d⁷ and d⁹ configurations. However, the CFSE gain is only Δ_o.

TABLE 13.11 Species forming square-planar complexes

<i>d electron configuration</i>	<i>Species</i>		<i>Approx. CFSE</i>	<i>Unpaired electrons</i>
d ⁸	Ni(II)	Pd(II)	2ΔE _{oct}	0
		Rh(I)	Ir(I)	
			Au(III)	
d ⁹	Cu(II)	Ag(II)	ΔE _{oct}	1 (in d _{x²-y²})
d ⁷	Co(II)		ΔE _{oct}	1 (in d _{xy})
d ⁶	Fe(II)		$\frac{1}{2}\Delta E_{\text{oct}}$	2
d ⁴	Cr(II)		$\frac{1}{2}\Delta E_{\text{oct}}$	4

The Cr(II) spin corresponds to one electron in each of the four stable orbitals, and the Fe(II) value indicates two filled and two half-filled orbitals. The CFSE are with respect to the octahedral configuration, those for d⁴ and d⁶ being for the weak field configuration.

- Table 13.11 lists the species which typically form square-planar complexes.
- While such *square complexes of the first-row elements are comparatively rare*, those formed by heavy transition elements are the majority of the representatives of these oxidation states, especially for the d⁸ configurations.
- *In configurations other than d⁸, the CFSE gain relative to octahedral is small, and most of these configurations are distorted in the octahedral case*, so it is often difficult to decide what has happened. *For example, copper(II) compounds often show four short bonds in a square plane with two longer ones, or even three sets of pairs of bonds with different lengths.*
- The distortion mentioned in the last paragraph arises whenever the d_{z²} and d_{x²-y²} orbitals are unequally occupied. If, for example, there is *one electron in the d_{z²} orbital*, ligands on the z axis are more shielded from the nuclear field than are ligands on the x and y axes. *The ligand-metal distances in the z direction are therefore shorter than those in the xy plane.* If the electron is, instead, in the d_{x²-y²} orbital the four distances in the xy plane are shorter. Such distortions, which are less simple than described here, are one manifestation of *the Jahn-Teller theorem, which states that if a system has unequally occupied, degenerate energy levels it will so distort as to raise the degeneracy.* Cases where distortions are expected are d⁴ high spin, d⁷ low spin and d⁹. *Distortions involving t_{2g} levels are normally too small to be detected.*

- Because the size of the d-orbital splitting, and hence the LFSE, depends on the ligand, it follows that a preference for octahedral coordination will be least pronounced for weak-field ligands.
- With strong-field ligands, low-spin complexes might be preferred and, although the situation is complicated by the pairing energy, the LFSE of a low-spin octahedral complex will be greater than that of a high-spin complex. **There will thus be a correspondingly greater preference for octahedral over tetrahedral coordination when the octahedral complex is low-spin.**
- *This preference for octahedral over tetrahedral coordination plays an important role in the solid state by influencing the structures that are adopted by d-metal compounds.*
- *This influence is demonstrated by the ways in which the different metal ions X and Y in spinels (of formula YY₂O₄) occupy the octahedral or tetrahedral sites.*

CFT Evidences/Applications

One of the earliest thermodynamic studies in support of CFT was published by Don McClure in 1959. McClure showed that the absolute magnitudes of the lattice enthalpies of the divalent metal halides from the first transition series depended on the CFSE of the metal ion, as shown in Figure 16.10.

- In general, *the lattice enthalpy increases across the series as a result of the decreasing size of the ionic radius that accompanies the increase in the effective nuclear charge.*
- However, *the actual lattice enthalpies do not fit to a smooth, linear progression across the row*. Instead, there are distinct peaks and valleys in the experimental data.
- ***Those d^n configurations having the smallest deviation from the expected linear trend occur for the d^0 , d^5 , and d^{10} electron configurations***, each of which has a CFSE= 0 (ignoring the pairing energy). Some ***of the larger deviations from the linear progression (which correspond to more stable lattice enthalpies)*** occur for the d^3 and d^8 electron configurations, which (not coincidentally) happen to have the largest CFSEs ($-1.2\Delta_o$).

$$\text{CFSE} = [(-0.4) * (\text{no. of electrons in } t_{2g})] + [(0.6) * (\text{no. of electrons in } e_g)]$$

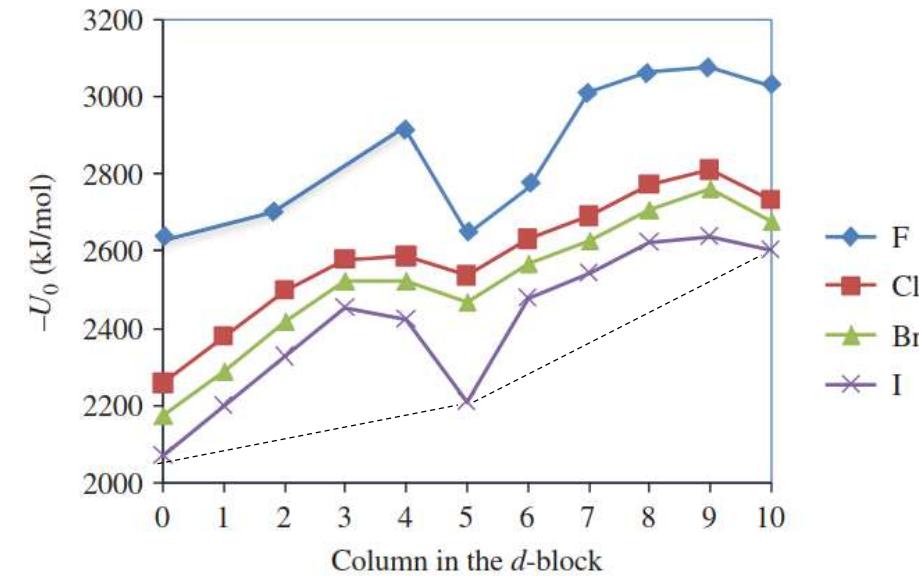


FIGURE 16.10. The absolute value of the magnitude of the lattice enthalpies (kJ/mol) for the divalent metal halides of the first transition series. [Data were obtained from <http://www.webelements.com> (accessed March 29, 2014)]. Thermochemical data were chosen over calculated values whenever they were known.]

- Other evidence for CFT comes from the **enthalpies of hydration** for the divalent metal ions of the first transition series. Again, a linear trend is expected, *the general trend to greater hydration enthalpy (more exothermic hydration) on crossing the period from left to right*. The experimental data are shown by the solid blue line in Figs. 16.11 and 20.7.
- The largest deviations from the expected trend occur for those d^n electron configurations having the greatest CFSE, namely d^3 and d^8 . If the CFSE is subtracted from the experimental enthalpy of hydration, the expected linear trend is observed, as shown by the solid red line.

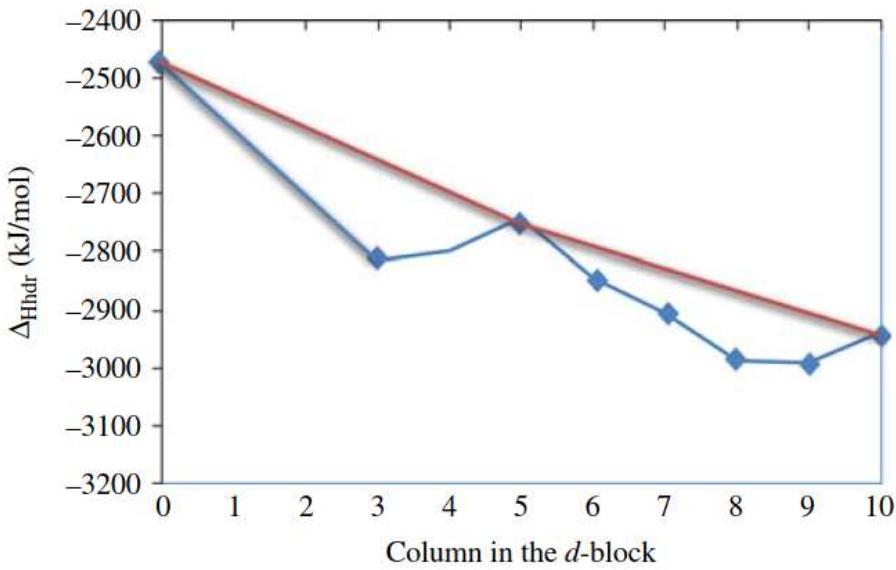


FIGURE 16.11
Hydration enthalpies for the first row divalent transition metals as a function of d^n electron count.
The blue line represents the experimental data, while the red line approximates the experimental values minus the CFSE.

The hydration enthalpy for the $2+$ ions is the enthalpy change for the reaction: $M^{2+} (g) + 6 H_2O \rightarrow [M(H_2O)_6]^{2+}$

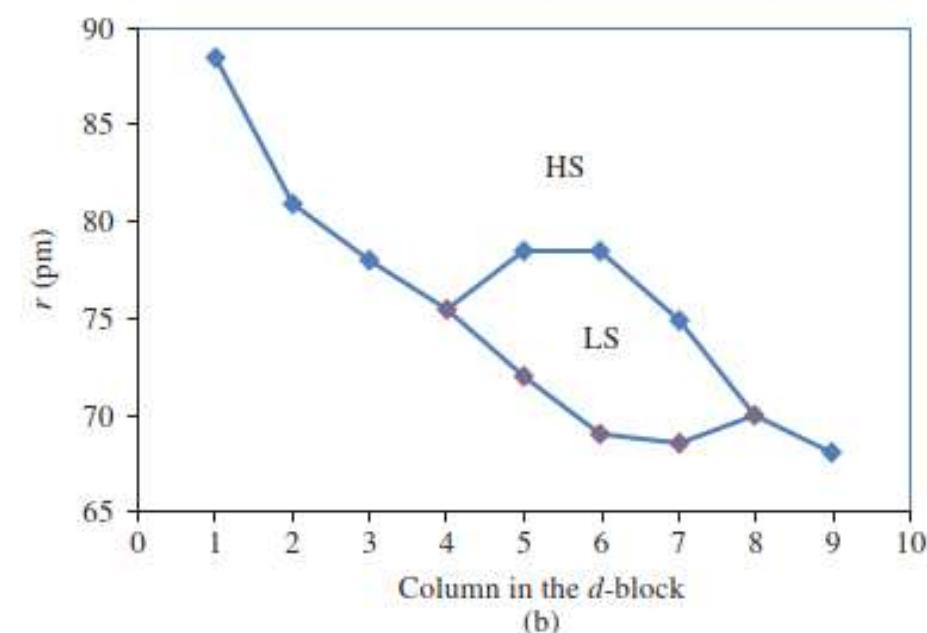
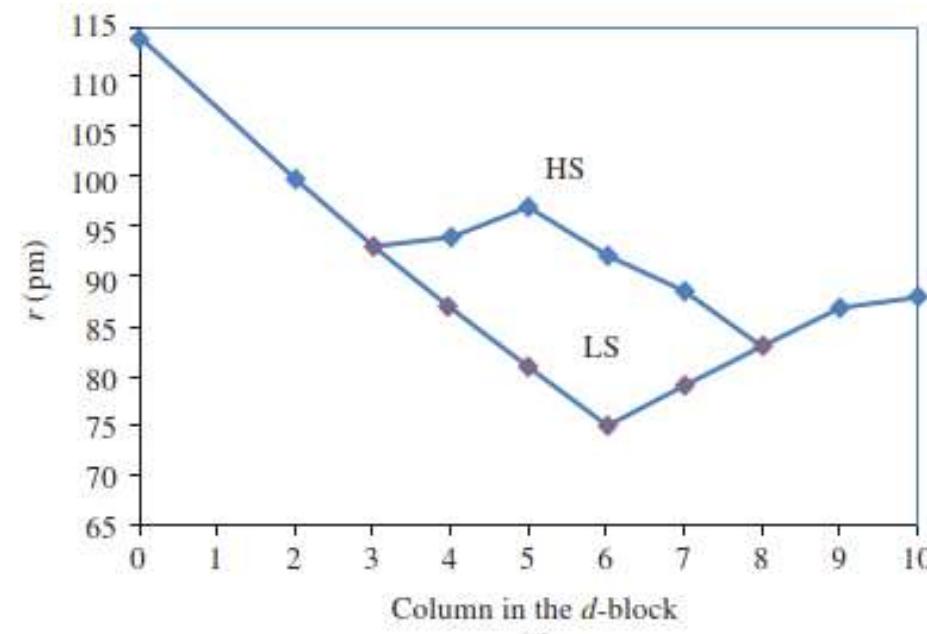


Figure 20.7 The hydration enthalpy of M^{2+} ions of the first row of the d block. The straight dotted lines show the trend when the crystal-field stabilization energy has been subtracted from the observed values.

Note the general trend to greater hydration enthalpy (more exothermic hydration) on crossing the period from left to right.

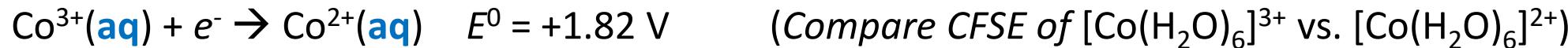
- With the advent of reliable X-ray crystallographic data, the **ionic radii** of the divalent and trivalent metal ions of the first transition series were reported by Shannon and Prewitt. In the case of coordination compounds having **LS** electron configurations, the **ionic radius decreases across the series as the t_{2g} set is filled until the d^6 electron configuration is reached**, as shown in Figure 16.12.
- The decrease across the row occurs (in part) because the **low-lying t_{2g} orbitals are somewhat bonding in nature**. Then, from d^7 to d^{10} , there is a gradual increase in the ionic radius as the higher lying, antibonding e_g set of orbitals is occupied. For the corresponding HS compounds, the radius decreases across the series until it reaches the d^3 configuration, where the t_{2g} orbitals are half-filled. The fourth and fifth electrons then occupy the antibonding e_g set and the ionic radius increases. It gradually decreases for d^6 – d^8 as the electrons again fill the more bonding t_{2g} level before finally increasing for d^9 and d^{10} as the e_g level is further occupied.

FIGURE 16.12. Ionic radii for divalent (a) and trivalent (b) first-row transition metal ions.
[Data were obtained from <http://www.webelements.com> (accessed March 29, 2014).]

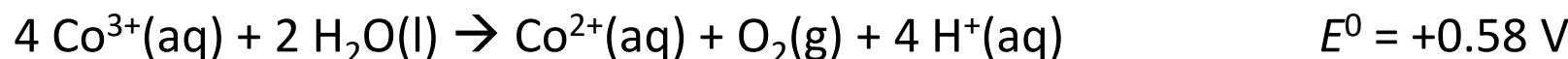


❖ CFSE: Stabilization of Oxidation States

The standard electrode potential for the reduction of Co(III) to Co(II) is



This large positive value suggests that Co^{3+} (aq) is a strong oxidizing agent, strong enough to oxidize water to O_2 (g)



Yet one of the complex ions, $[\text{Co}(\text{NH}_3)_6]^{3+}$, is stable in water solution, even though it contains cobalt in the +3 oxidation state. **$[\text{Co}(\text{NH}_3)_6]^{2+}$ is easily oxidized to Co(III) complex. On the other hand, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is a stable complex.**

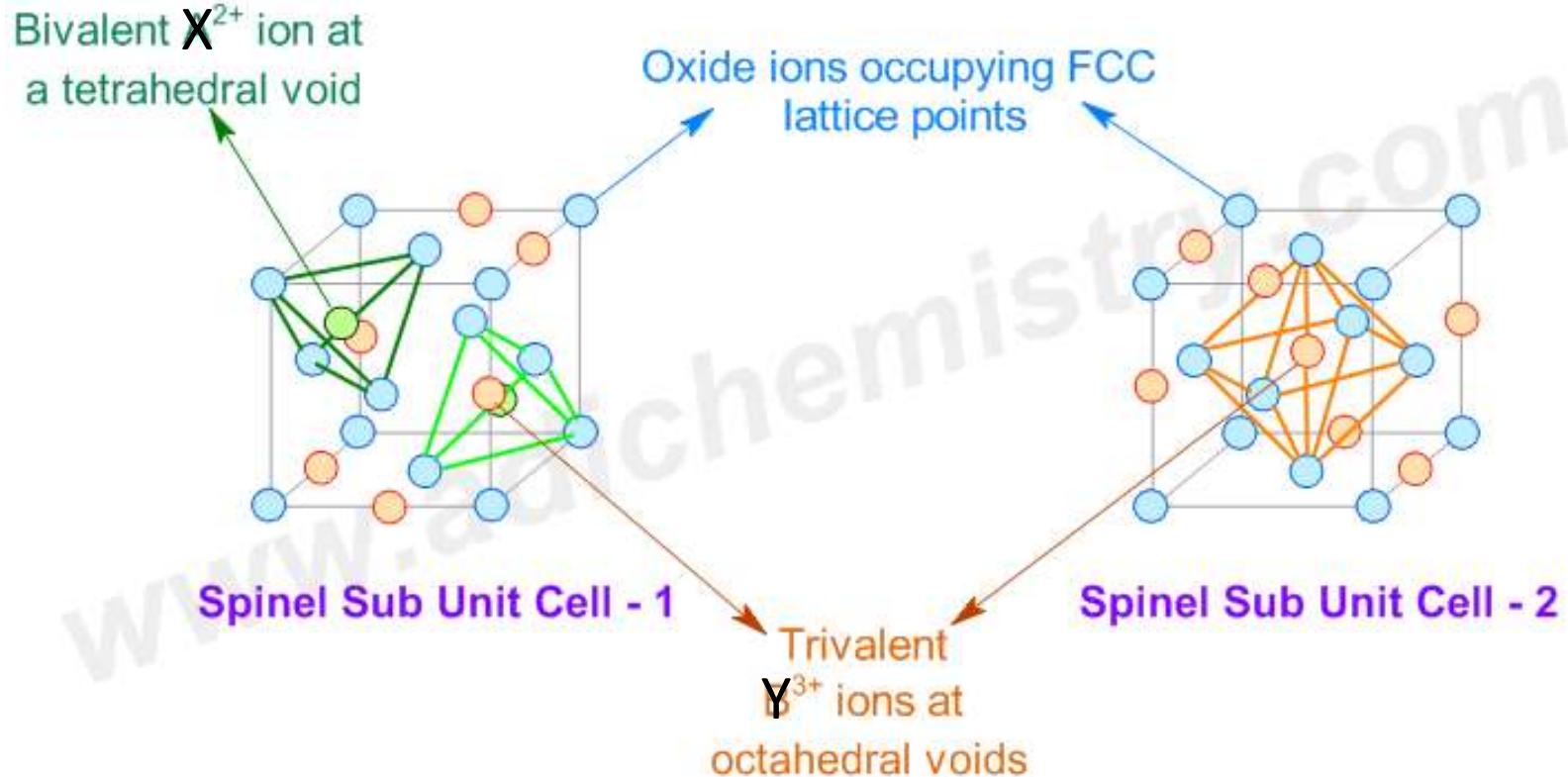
This phenomenon can be explained as follows:

- Co^{2+} is a d^7 electron system whereas Co^{3+} is a d^6 one.
- **H_2O is a weak field ligand, and we expect a high spin (HS) complex** with it. The HS d-electron configuration for d^7 and d^6 are, respectively: $t_{2g}^5e_g^2$ and $t_{2g}^4e_g^2$. The crystal field stabilization energy (CFSE) is higher for $t_{2g}^5e_g^2$ configuration, i.e., d^7 and hence **Co^{2+} is preferred** for the ligand, H_2O .
- On the other hand, **NH_3 is a strong field ligand, and we expect a low spin (LS) complex** with it. The LS d-electron configurations for d^7 and d^6 are: $t_{2g}^6e_g^1$ and t_{2g}^6 respectively. The crystal field stabilization energy (CFSE) is higher for the t_{2g}^6 configuration, i.e., **d^6 and hence Co^{3+} is preferred** for the ligand, NH_3 .
- **The ability of a strong electron-pair donor** (strong Lewis base) to stabilize high oxidation states in the way that NH_3 does in Co(III) complexes and O^{2-} in Mn(VII) complexes (such as MnO_4^-) **affords a means of attaining certain oxidation states that might otherwise be difficult or impossible to attain**.

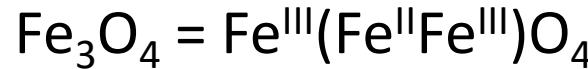
❖ Mixed metal oxides

- Spinel, MgAl_2O_4 , has a structure in which Mg^{2+} occupy 1/8 of the tetrahedral cavities and Al^{3+} 1/2 of the octahedral cavities of a ccp array of oxygen atoms.
- Among the oxides of composition $\text{X}^{2+}\text{Y}_2^{3+}\text{O}_4$ (X^{2+} are Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn, and Y^{3+} are Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Ni, and Rh), those in which the *tetrahedral holes are occupied by X^{2+}* are called **normal spinels** (or by Y^{3+} are called **inverse spinels**, respectively).
- Spinel itself has a normal spinel-type structure.
- MgFe_2O_4 and Fe_3O_4 have inverse spinel-type structures.
- ***Crystal field stabilization energies differ depending on whether the crystal field of the oxygen atoms is a regular tetrahedron or octahedron.***
- Therefore, ***when the metal component is a transition metal, the energy difference is one of the factors to determine which of X^{2+} or Y^{3+} is favorable to fill the tetrahedral cavities.***

➤ A **normal spinel** can be represented as: $(X^{II})^{tet}(Y^{III})_2^{oct}O_4$, where: X^{II} = a divalent cation (like Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn) and Y^{III} = a trivalent cation (like Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Ni) and X (a weak-field ligand) = O, S, Se, etc.



- A ***normal spinel*** structure is assumed if both divalent and trivalent metals are **nontransition metals** since **no CFSE** is involved.
- Usually d³ & d⁸ ions have **strongest preference for octahedral geometry**. There is a tendency of formation of ***inverse spinel structure*** in some cases (not all the cases) which contain transition metal ions. This is because, the transition metal ion **may get extra stability (LFSE) in octahedral geometry** and prefers octahedral voids over tetrahedral ones. That means, if X^{II} has d³ or d⁸ configuration and the Y^{III} ion has configuration other than these, then the **spinel** is inverted.
- An ***inverse spinel*** can be represented as: (Y^{III})^{tet}(X^{II})^{oct}(Y^{III})^{oct}O₄
- ✓ Examples of ***Inverse spinels***: Fe₃O₄ (ferrite), CoFe₂O₄, NiFe₂O₄, etc.
- ✓ The above ***inverse spinels*** can also be written as:



Rules:

1. If both A^{+2} and B^{+3} are non-transition metals, then spinel will be NORMAL.
2. If A^{+2} is non-transition metal and B^{+3} is transition metal (with $d^1 d^2 d^3 d^4 d^6 d^7 d^8 d^9$) then spinel will be NORMAL.
3. If A is transition metal with ($d^1 d^2 d^3 d^4 d^6 d^7 d^8 d^9$) and B is also transition metal with ($d^0 d^5$ and d^{10}) system, then spinel will be INVERSE.

A^{II}	B^{III}	Structure
Non transition metal or d^0 or d^5 or d^{10} transition metal	Non transition metal	Spinel structure
Non transition metal or d^0 or d^5 or d^{10} transition metal	A transition metal with d^1 or d^2 or d^3 or d^4 or d^6 or d^7 or d^8 or d^9 configurations	Spinel structure
A transition metal with d^1 or d^2 or d^3 or d^4 or d^6 or d^7 or d^8 or d^9 configurations	Non transition metal or transition meta with d^0 or d^5 or d^{10} configurations	Inverse spinel
Transition metal with higher CFSE value	Transition metal with lower CFSE value	Inverse spinel

MAGNETIC MEASUREMENTS

Key points: *Magnetic measurements are used to determine the number of unpaired spins in a complex* and hence to identify its ground-state configuration. A spin-only calculation may fail for low-spin d⁵ and for high-spin 3d⁶ and 3d⁷ complexes.

The experimental distinction between high-spin and low-spin octahedral complexes is based on the determination of their magnetic properties. Compounds are classified as diamagnetic if they are repelled by a magnetic field and paramagnetic if they are attracted by a magnetic field. The two classes are distinguished experimentally by magnetometry. The *magnitude of the paramagnetism of a complex is commonly reported in terms of the magnetic dipole moment* it possesses: the higher the magnetic dipole moment of the complex, the greater the paramagnetism of the sample.

In a free atom or ion, both the orbital and the spin angular momenta give rise to a magnetic moment and contribute to the paramagnetism. The following formula for the magnetic moment (μ) of a molecule in Bohr magnetons is:

$$\mu_{\text{total}} = -[\{L(L + 1)\} + 4\{S(S + 1)\}]^{1/2} \mu_B$$

When *the atom or ion is part of a complex, any orbital angular momentum is normally quenched, or suppressed*, as a result of the interactions of the electrons with their nonspherical environment. However, if any electrons are unpaired, *the net electron spin angular momentum survives* and gives rise to **spin-only paramagnetism**, which is characteristic of many d-metal complexes. The spin-only magnetic moment, μ , of a complex with total spin quantum number S is:

$$\mu = 2\{S(S + 1)\}^{\frac{1}{2}} \mu_B \quad (20.1)$$

where μ_B is the Bohr magneton, $\mu_B = e\hbar/2m_e$ with the value 9.274×10^{-24} J T⁻¹. Because **S = N/2**, where *N is the number of unpaired electrons*, each with spin $s = 1/2$,

$$\mu = \{N(N + 2)\}^{\frac{1}{2}} \mu_B \quad (20.2)$$

- Based on Hund's rule, electrons occupy orbitals of equal energy one at a time. When all lower energy orbitals are half-filled, the next electron can enter a half-filled orbital and pair up by overcoming a repulsive pairing energy (E_{pairing}).
- The next electron can enter an empty, higher energy orbital by overcoming Δ (crystal field splitting energy).
- Thus, the relative sizes of E_{pairing} and Δ determine the occupancy of d orbitals, which determines the number of unpaired electrons and, thus, the magnetic behavior of the ion.
- A measurement of the magnetic moment of a d-block complex can usually be interpreted in terms of the number of unpaired electrons it contains, and hence it is possible to tell whether a complex is high or low spin by examining its magnetic behavior.
- For example, magnetic measurements on a d⁶ complex easily distinguish between a high-spin t_{2g}⁴ e_g² (N = 4, S = 2, $\mu = 4.90\mu_B$) configuration and a low-spin t_{2g}⁶ (N = 0, S = 0, $\mu = 0$) configuration.
- ✓ The high-spin complex [Fe(H₂O)₆]²⁺ has four unpaired electrons and is paramagnetic (*attracted by a magnet*), whereas the low-spin [Fe(CN)₆]⁴⁻ complex has no unpaired electrons and is diamagnetic (*repelled by a magnet*).

❖ **Test:** The magnetic moment of the complex $[\text{Mn}(\text{NCS})_6]^{4-}$ is $6.06 \mu_B$. What is its d-electron configuration?

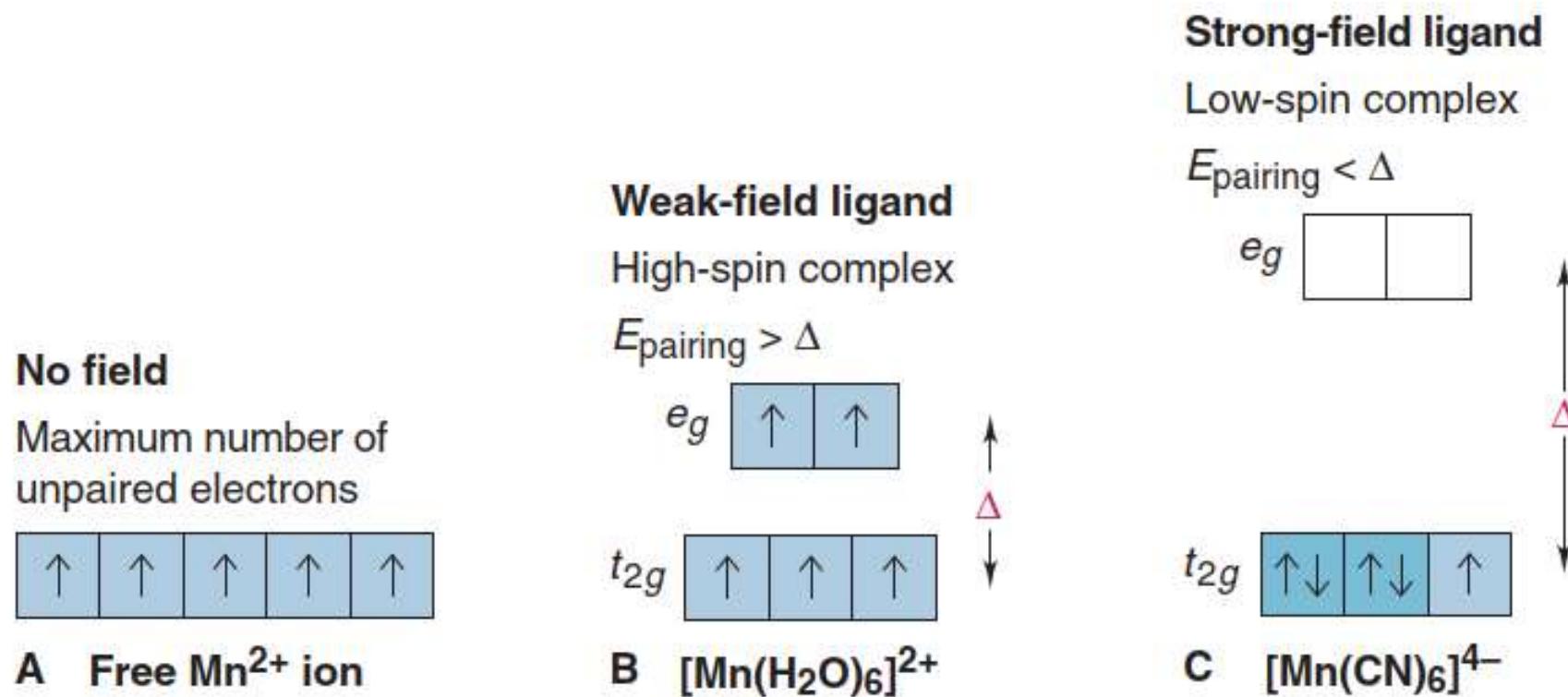


Figure 22.22 High-spin and low-spin octahedral complex ions of Mn^{2+} . A: Free Mn^{2+} has five unpaired electrons. B: Bonded to a weak-field ligand, Mn^{2+} still has five unpaired electrons (high-spin complex). C: Bonded to a strong-field ligand, Mn^{2+} has one unpaired electron (low-spin complex).

- The spin-only magnetic moments for some electron configurations are listed in Table 20.3 and compared there with experimental values for a number of 3d complexes.
- For most 3d complexes (and some 4d complexes), experimental values lie reasonably close to spin-only predictions, so it becomes possible to identify correctly the number of unpaired electrons and assign the ground-state configuration.
- For instance, $[\text{Fe}(\text{OH}_2)_6]^{3-}$ is paramagnetic with a magnetic moment of $5.9\mu_B$. As shown in Table 20.3, this value is consistent with there being five unpaired electrons ($N = 5$ and $S = 5/2$), which implies a high-spin $t_{2g}^3 e_g^2$ configuration.

Table 20.3 Calculated spin-only magnetic moments

Ion	Electron configuration	S	μ/μ_B Calculated	Experimental
Ti ³⁺	t_{2g}^1	$\frac{1}{2}$	1.73	1.7–1.8
V ³⁺	t_{2g}^2	1	2.83	2.7–2.9
Cr ³⁺	t_{2g}^3	$\frac{3}{2}$	3.87	3.8
Mn ³⁺	$t_{2g}^3 e_g^1$	2	4.90	4.8–4.9
Fe ³⁺	$t_{2g}^3 e_g^2$	$\frac{5}{2}$	5.92	5.9

Table 7.3 Calculated magnetic moments, in Bohr magnetons, of the ground states of some free transition-metal ions and the experimental magnetic moments for the octahedrally co-ordinated ions in their high-spin configurations

Ion	S	L	n	n'	μ_S	μ_{total}	μ_{exp}
Ti ³⁺	$\frac{1}{2}$	2	1	1	1.73	3.00	1.7 – 1.8 [†]
V ⁴⁺	$\frac{1}{2}$	2	1	1	1.73	3.00	1.7 – 1.8 [†]
V ³⁺	1	3	2	2	2.83	4.47	2.6 – 2.8 [†]
Cr ³⁺	$\frac{3}{2}$	3	3	3	3.87	5.20	3.7 – 3.9
Cr ²⁺	2	2	4	4	4.90	5.48	4.7 – 4.9
Mn ³⁺	2	2	4	4	4.90	5.48	4.9 – 5.0
Mn ²⁺	$\frac{5}{2}$	0	5	5	5.92	5.92	5.6 – 6.1
Fe ³⁺	$\frac{5}{2}$	0	5	5	5.92	5.92	5.7 – 6.0
Fe ²⁺	2	2	6	4	4.90	5.48	5.1 – 5.5 [†]
Co ³⁺	2	2	6	4	4.90	5.48	ca. 5.4 [†]
Co ²⁺	$\frac{3}{2}$	3	7	3	3.87	5.20	4.1 – 5.2 [†]
Ni ²⁺	1	3	8	2	2.83	4.47	2.8 – 3.5
Cu ²⁺	$\frac{1}{2}$	2	9	1	1.73	3.00	1.7 – 2.2

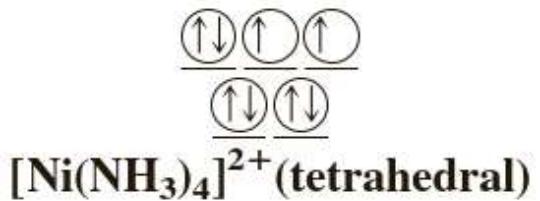
[†]The configurations marked † are those for which there can be an orbital contribution to the magnetic moment, see text. n = number of d electrons, n' = number unpaired.

H.L. Schläfer and G. Gliemann, *Basic Principles of Ligand Field Theory*. © 1969, John Wiley & Sons Ltd; reprinted with permission.

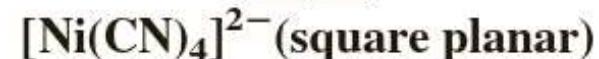
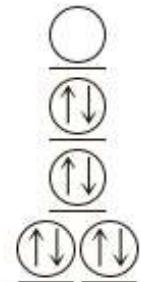
Describe the d-electron distributions of the complexes $[\text{Ni}(\text{NH}_3)_4]^{2+}$ and $[\text{Ni}(\text{CN})_4]^{2-}$, according to crystal field theory. The tetraamminenickel(II) ion is *paramagnetic*, and the tetracyanonickelate(II) ion is *diamagnetic*.

....The complex ions given in the problem are 4 C.N.: ***either tetrahedral or square planar.***

➤ **The tetrahedral field to give high-spin complexes and the square planar field to give low-spin complexes.** Therefore, the geometry of the $[\text{Ni}(\text{NH}_3)_4]^{2+}$ ion, which is paramagnetic (8 electrons are **NOT** paired), is probably tetrahedral. The distribution of d electrons in the Ni^{2+} ion (configuration d^8) is:



The geometry of $[\text{Ni}(\text{CN})_4]^{2-}$, which is diamagnetic (all 8 electrons are **paired**), is probably square planar; the distribution of d electrons is:



Q. Predict the number of unpaired spins in the $[\text{Cr}(\text{en})_3]^{2+}$ ion. Calculate magnetic moment.

Strategy The magnetic properties of a complex ion depend on the *strength of the ligands*. Strong-field ligands cause a high degree of splitting among the d orbital energy levels, resulting in low-spin complexes. Weak-field ligands, which cause a small degree of splitting among the d orbital energy levels, result in high-spin complexes.

Solution

The electron configuration of Cr^{2+} is $[\text{Ar}]3\text{d}^4$. Because *en is a strong-field ligand*, we expect $[\text{Cr}(\text{en})_3]^{2+}$ to be a low-spin complex. All four electrons will be placed in the lower-energy d orbitals (d_{xy}^2 , d_{yz}^1 , and d_{xz}^1) and there will be *two unpaired spins* and hence paramagnetic complex.

➤ But the *complex ion is diamagnetic*. Use *ideas from the crystal field theory to speculate on its probable structure*.

- The interpretation of magnetic measurements is sometimes less straightforward than the above examples might suggest.
- ✓ For example, the potassium salt of $[\text{Fe}(\text{CN})_6]^{3-}$ has $\mu = 2.3\mu_B$, which is between the spin-only values for one and two unpaired electrons ($1.7\mu_B$ and $2.8\mu_B$, respectively). In this case, the spin-only assumption has failed because the orbital contribution to the magnetic moment is substantial.

□ Optical Properties of Coordination Complexes

❖ A solution of CuSO_4 (in fact, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$) appears blue. Why?

Origin of Color?

White light consists of all wavelengths (λ) in the visible range and can be dispersed into colors of a narrower wavelength range.

Objects appear colored in white light because they absorb only certain wavelengths: an opaque object reflects the other wavelengths, and a clear one transmits them. If an object absorbs all visible wavelengths, it appears black; if it reflects all, it appears white.

Each color has a complementary color; for example, green and red are complementary colors. Figure 22.15 shows these relationships on an artist's color wheel in which complementary colors are wedges opposite each other. *A mixture of complementary colors absorbs all visible wavelengths and appears black.*

An object has a particular color for one of two reasons:

- It **reflects** (or **transmits**) light of that color. Thus, if an object absorbs all wavelengths except green, the reflected (or transmitted) light is seen as green.
- It **absorbs** light of the *complementary color*. Thus, if the object absorbs only red, the complement of green, the remaining mixture of reflected (or transmitted) wavelengths is also seen as green.

❖ A solution of $CuSO_4$ appears blue to us. Why?

❖ Consider the hydrated cupric ion, $[Cu(H_2O)_6]^{2+}$, which *absorbs light in the orange region of the spectrum so that a solution of $CuSO_4$ appears blue to us.*

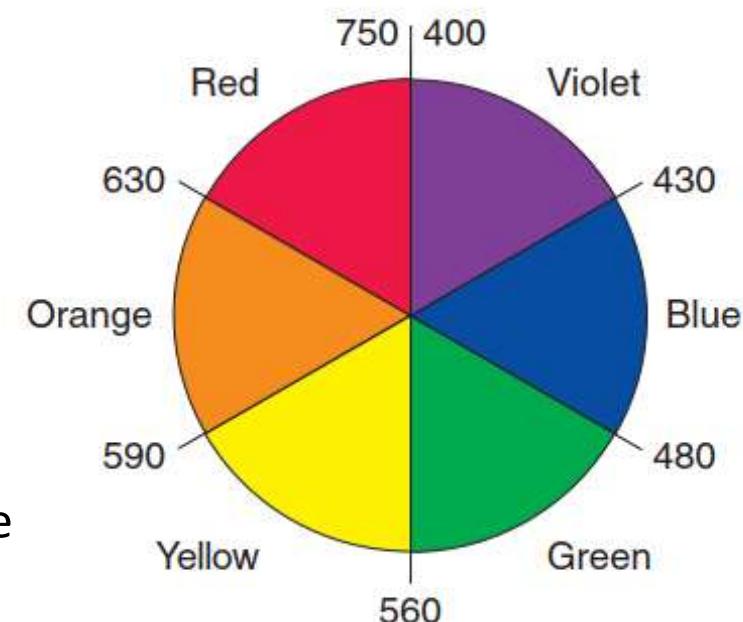


Figure 22.15 An artist's wheel. Colors, with approximate wavelength ranges (in nm), are shown as wedges.

Table 22.9 lists the color absorbed and the resulting color observed.

Table 22.9 Relation Between Absorbed and Observed Colors

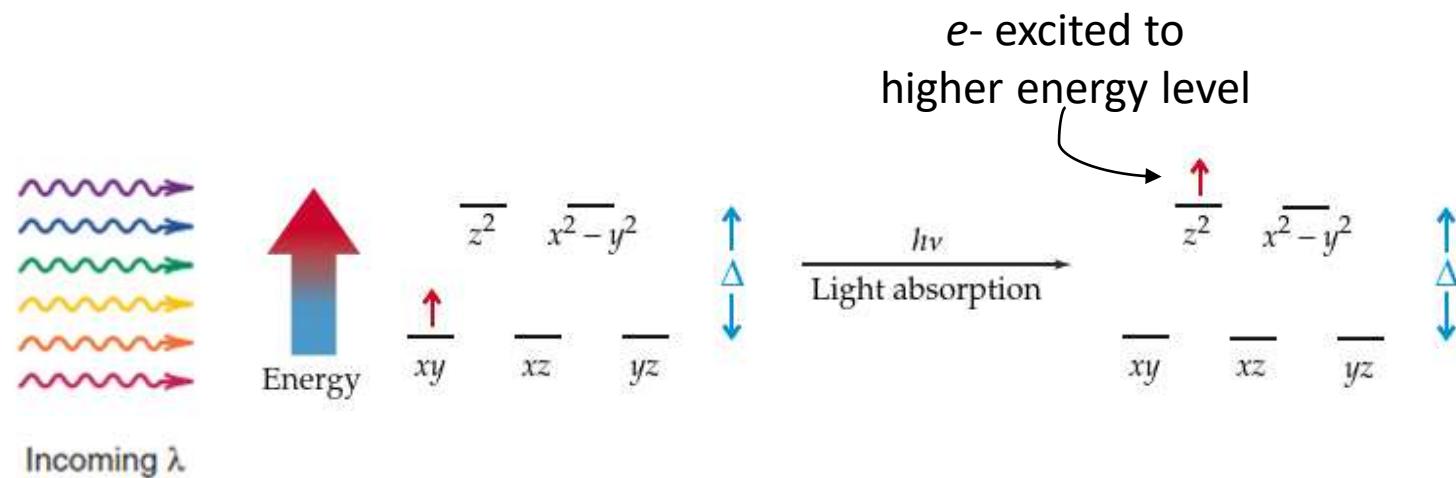
Absorbed Color	λ (nm)	Observed Color	λ (nm)
Violet	400	Green-yellow	560
Blue	450	Yellow	600
Blue-green	490	Red	620
Yellow-green	570	Violet	410
Yellow	580	Dark blue	430
Orange	600	Blue	450
Red	650	Green	520

□ Optical Properties of Coordination Complexes

❖ THE ELECTRONIC SPECTROSCOPY OF TRANSITION-METAL COMPLEXES

- No account of the theory of the transition-metal ions would be complete without some reference to their electronic spectroscopy. But this is a vast and complicated subject which is well treated in a number of specialist volumes and here we can only draw attention to a few significant points.
- When a coordination complex absorbs light, an electron is excited from a d orbital of lower energy to a d orbital of higher energy. The larger the Δ , the smaller the wavelength of the absorbed light. In the case of an octahedral complex, absorption of light would excite an electron from a t_{2g} to an e_g orbital.

Fig... When a light wave hits a d-orbital electron, the electron may absorb the energy and jump to a higher energy orbital. The rest of the light wave transmits out of the sample.



- A d-to-d ($d \rightarrow d$) transition must occur for a transition metal complex to show color. Therefore, ions with d^0 or d^{10} electron configurations are usually colorless.
- ✓ Compare the colors of aq. CuSO_4 and aq. ZnSO_4 . Explain the origin of the difference.
- UV-Vis spectroscopy is an analytical chemistry technique used to study the optical properties of various transition metal compounds. UV-Vis spectroscopy works by exciting a metal's d-electron from the ground state configuration to an excited state using UV-visible light. In short, when energy in the form of light is directed at a transition metal complex, a d-electron will gain energy and a UV-Vis spectrophotometer measures the absorbance light by the transition metal complexes with excited electrons at a specific wavelength of light, from the visible light region to the UV region.
- When using a UV-Vis Spectrophotometer, the solution to be analyzed is prepared by placing the sample in a cuvette then placing the cuvette inside the spectrophotometer. The machine then shines light waves from the visible and ultraviolet wavelengths and measures how much light of each wavelength the sample absorbs and then emits.
- Absorbance of the sample can be calculated via Beer's Law: $A = \epsilon Ic$, where A is the absorbance, ϵ is the molar absorptivity of the sample, I is the length of the cuvette used, and c is the concentration of the sample. When the spectrophotometer produces the absorption graph, the molar absorptivity can then be calculated. To illustrate how this absorption graph looks like, you will find a sample absorbance spectrum below. As can be seen, the y-axis represents absorbance (A) and the x-axis represents the wavelengths of light being scanned. This specific transition metal complex, $[\text{CrCl}(\text{NH}_3)_5]^{2+}$, has the highest absorbance in the UV region of light, right around 250-275 nm, and two slight absorbance peaks near 400 nm and 575 nm respectively. The two latter peaks are much less pronounced than the former peak due to the **electron's transition being partially forbidden**—a concept that will be discussed later in this section. If a transition is forbidden, not many transition metal electrons will undergo the excitation.

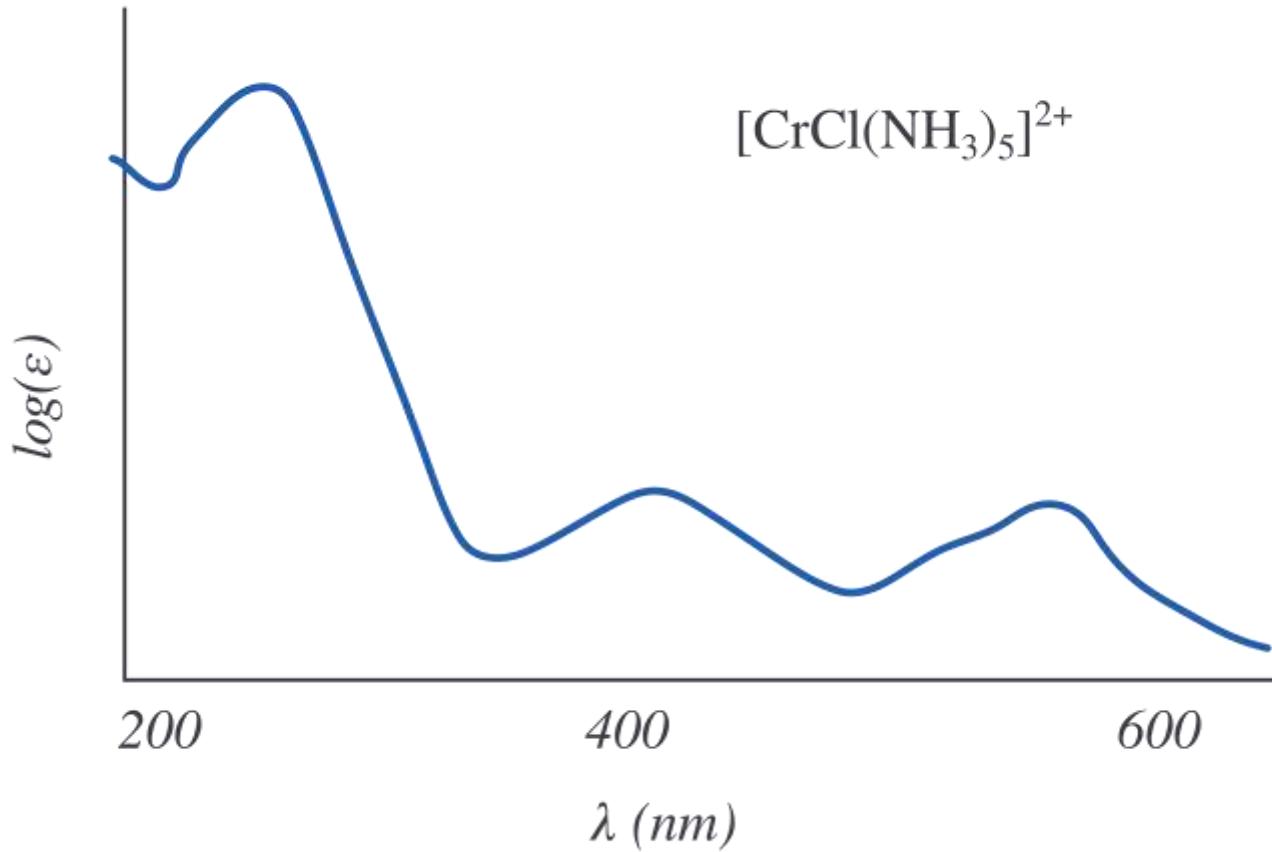


Figure 1.16.1: UV-Vis Spectrum of a Chromium(III) complex.

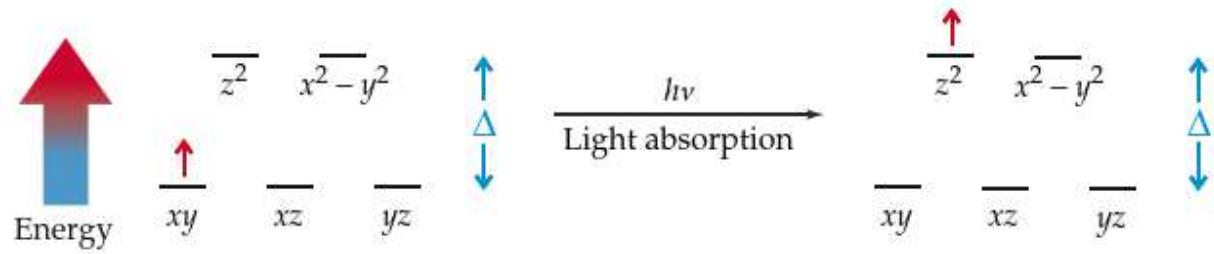
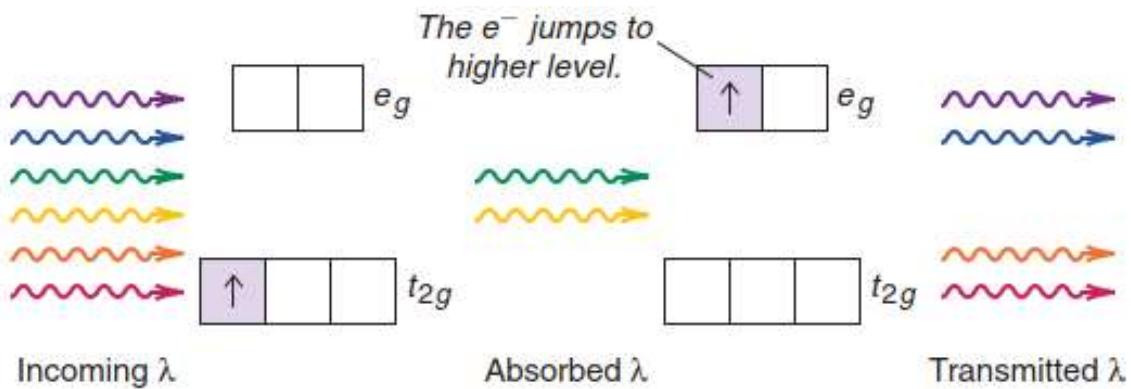
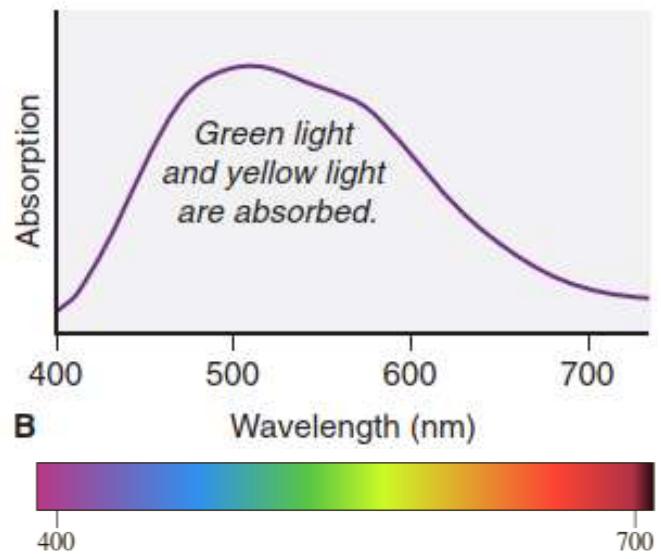


Figure 22.19 The color of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$.

A: The hydrated Ti^{3+} ion shows purple color.

B: An absorption spectrum shows that **green light** and **yellow light** are absorbed and other wavelengths are transmitted.

C: The process of photon absorption. An orbital diagram depicts the light colors absorbed when the d electron jumps to the higher level when the energy of the incoming photon is equal to the crystal field splitting. The **maximum absorption peak** in the visible region occurs at $\sim 498 \text{ nm}$.

- We have been drawn into consideration of electronic spectra because *spectral data provide the most direct way of determining the crystal field splitting, Δ , (d -orbital splitting) energy, the essential parameters of the CF model.*
- For example, an octahedral $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ complex has a smaller Δ compared to an octahedral $[\text{Cr}(\text{CN})_6]^{4-}$ complex (Fig. 7.1.16), and thus the aqua complex absorbs light of longer wavelength compared to the cyano complex. Vice versa, measuring the absorption spectra of the complexes, allows us to make statements about the relative crystal field strength of the ligands.
- By measuring the absorption spectrum of many complexes with a variety of ligands we can develop a so-called ***spectrochemical series*** that orders ligands according to their field strength.

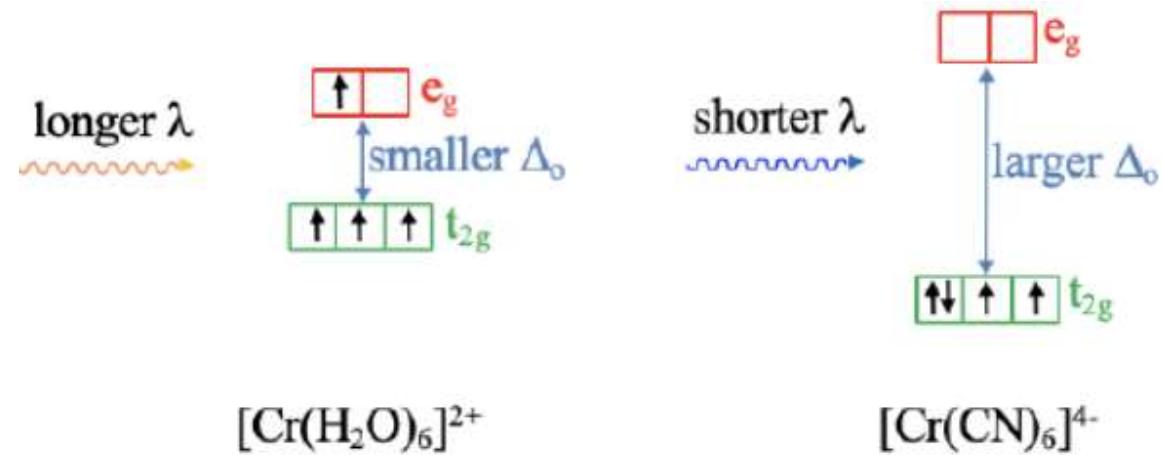


Figure 7.1.16 Octahedral $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ complex compared to an octahedral $[\text{Cr}(\text{CN})_6]^{4-}$ complex

❖ Explaining the Colors of Transition Metal Complexes:

- The color of a coordination compound is determined by Δ of its complex ion. When the ion absorbs radiant energy, electrons can move from the lower energy level to the higher energy level (say, t_{2g} to e_g). Recall that the ***difference between two energy levels is equal to the energy (and inversely related to the wavelength) of the absorbed photon:***

$$\Delta E_{\text{electron}} = E_{\text{photon}} = h\nu = hc/\lambda$$

- Consider the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion, which appears **purple** in aqueous solution (Figure 22.19, see below).
- Hydrated Ti^{3+} has its ***one d electron*** in one of the three lower energy t_{2g} orbitals.
- The energy difference (Δ) between the t_{2g} and e_g orbitals in this ion corresponds to photons between the green and yellow range. When white light shines on the solution, these colors of light are absorbed, and the electron jumps to one of the e_g orbitals.
- Red, blue, and violet light are transmitted, so the solution appears purple.

- The best way to measure crystal field splitting is to use spectroscopy to determine the wavelength at which light is absorbed. The $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion provides a straightforward example, because Ti^{3+} has only one 3d electron (Figure 20.14). The $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion absorbs light in the visible region of the spectrum (Figure 20.15). The wavelength corresponding to maximum absorption is 498 nm [Figure 20.14(b)]. This information enables us to calculate the crystal field splitting as follows. We start by writing:

$$\Delta = h\nu$$

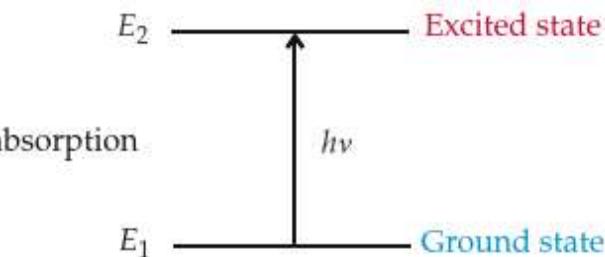
(20.1)

Also

$$\nu = \frac{c}{\lambda}$$

where c is the speed of light and λ is the wavelength. Therefore,

$$\begin{aligned}\Delta &= \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(498 \text{ nm})(1 \times 10^{-9} \text{ m}/1 \text{ nm})} \\ &= 3.99 \times 10^{-19} \text{ J}\end{aligned}$$



Equation (7.3) shows that $E = hc/\lambda$.

This is the energy required to excite *one* $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion. To express this energy difference in the more convenient units of kilojoules per mole, we write

$$\begin{aligned}\Delta &= (3.99 \times 10^{-19} \text{ J/ion})(6.02 \times 10^{23} \text{ ions/mol}) \\ &= 240,000 \text{ J/mol} \\ &= 240 \text{ kJ/mol}\end{aligned}$$

The Spectrochemical Series:

- The fact that *color depends on the ligand* allows us to create a spectrochemical series, which ranks the ability of a ligand to split d-orbital energies (Figure 22.21). Using this series, we can predict the relative magnitude of Δ for a series of octahedral complexes of a given metal ion.
 - ✓ Although we cannot predict the actual color of a given complex, we can determine whether a complex will absorb longer or shorter wavelengths than other complexes in the series.

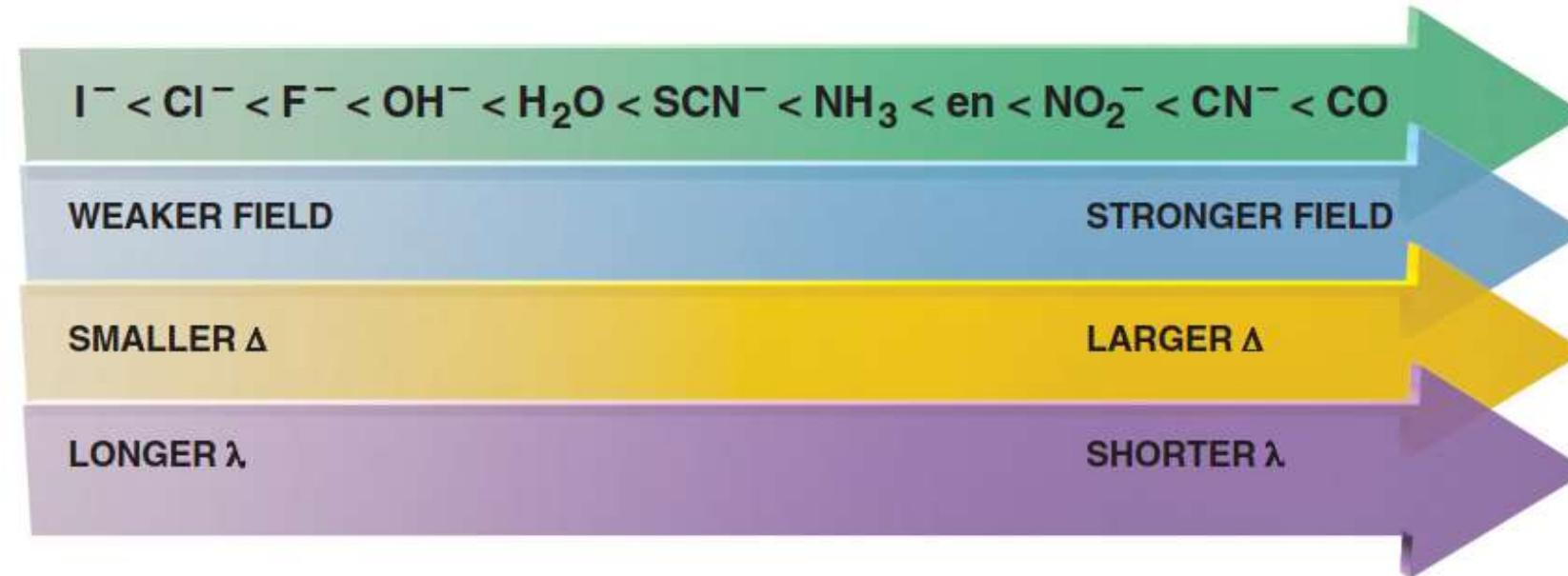


Figure 22.21 The spectrochemical series. As Δ increases, shorter wavelengths (higher energies) of light must be absorbed to excite electrons. For reference, water is a weak-field ligand.

- We can see for example, that an aqua ligand is a stronger field ligand compared to a fluoro ligand, but a weaker ligand than an ammine ligand.
- Generally, ligands at the left end of the series produce weaker fields, smaller Δ , and absorb light with longer wavelengths. Ligands at the right end of the series produce stronger fields, create larger Δ , and absorb light of shorter wavelengths.
- However, ***crystal filed theory*** ***cannot explain different ligand strength***. Why does one ligand produce a stronger field than another?
- To answer this question, we need the ligand field theory.

- Absorption spectra can show the wavelengths absorbed by: (1) a metal ion with different ligands and (2) different metal ions with the same ligand.
- Such data allow us to relate the energy of the absorbed light to Δ and make two key observations:
 - **For a given ligand, color depends on the oxidation state of the metal ion.** In Figure 22.20A, aqueous $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ (left) is violet and $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ (right) is yellow.
 - **For a given metal ion, color depends on the ligand.** A single ligand substitution can affect the wavelengths absorbed and, thus, the color (Figure 22.20B).

Figure 22.20 Effects of *oxidation state* and *ligand* on color.

A: Solutions of two hydrated vanadium ions: O.N. of V is +2 (left); O.N. of V is +3 (right).

B: A change in one *ligand can influence the color*. $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is yellow (left), and $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ is purple (right).



➤ The absorption spectra of different complexes indicate that the *size of the crystal field splitting depends on the nature of the ligands*. For example, Δ for Ni^{2+} ($[\text{Ar}] \ 3\text{d}^8$) complexes increases as the ligand varies from H_2O to NH_3 to ethylenediamine (en). Accordingly, the electronic transitions shift to higher energy (shorter wavelength) as the ligand varies from H_2O to NH_3 to en, thus accounting for the observed variation in color (Figure 20.24):

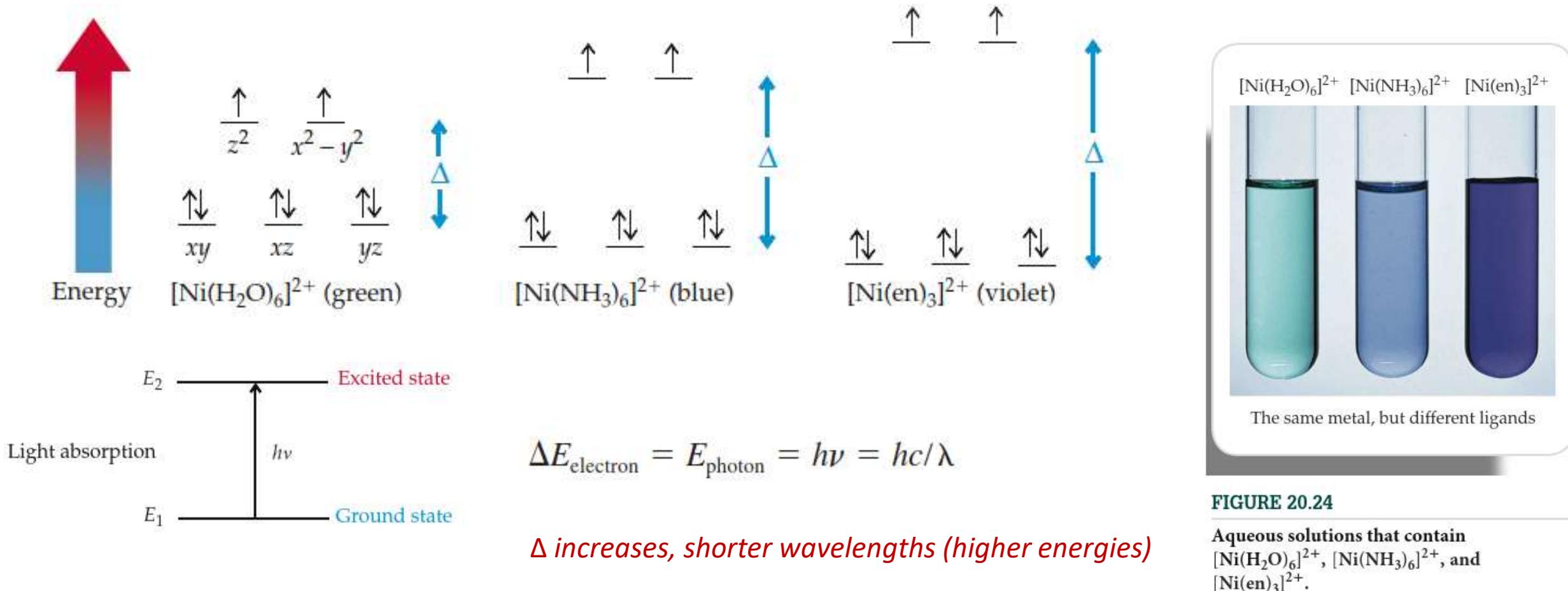


FIGURE 20.24

Aqueous solutions that contain $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, and $[\text{Ni}(\text{en})_3]^{2+}$.

Ranking Crystal Field Splitting Energies (Δ) for Complex Ions of a Metal

Problem Rank $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Ti}(\text{CN})_6]^{3-}$, and $[\text{Ti}(\text{NH}_3)_6]^{3+}$ in terms of Δ and of the energy of visible light absorbed.

Plan The formulas show that Ti has an oxidation state of +3 in the three ions. From Figure 22.21, we rank the ligands by crystal field strength: the stronger the ligand, the greater the splitting, and the higher the energy of light absorbed.

Solution The ligand field strength is in the order $\text{CN}^- > \text{NH}_3 > \text{H}_2\text{O}$, so the relative size of Δ and energy of light absorbed is



FOLLOW-UP PROBLEM 22.4 Which complex ion absorbs visible light of higher energy, $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ or $[\text{V}(\text{NH}_3)_6]^{3+}$?

❖ REVIEW OF CONCEPTS

The Cr^{3+} ion forms octahedral complexes with two neutral ligands X and Y. The color of $[\text{CrX}_6]^{3+}$ is blue while that of $[\text{CrY}_6]^{3+}$ is yellow. Which is a stronger field ligand?

Q. The color of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ is violet whereas that of $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ is yellow. Explain this difference in color.

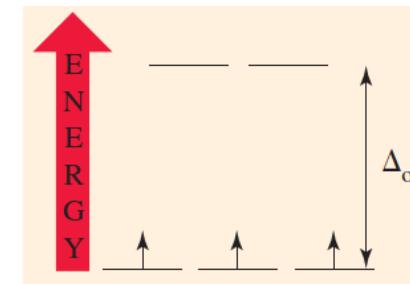
....Both chromium(III) complexes are octahedral, and the electron configuration of Cr^{3+} is $[\text{Ar}]d^3$. From these facts, we can construct the energy-level diagram shown here. The three unpaired electrons go into the three lower-energy d orbitals. When a photon of light is absorbed, an electron is promoted from a d orbital of lower energy to a d orbital of higher energy. The quantity of energy required for this promotion depends on the energy level separation, Δ_o .

According to the spectrochemical series, NH_3 produces a greater splitting of the d energy level than does H_2O .

We should expect $[\text{Cr}(\text{NH}_3)_6]^{3+}$ to absorb light of a shorter wavelength (higher energy) than does $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$.

Thus, $[\text{Cr}(\text{NH}_3)_6]^{3+}$ absorbs in the violet region of the spectrum, and the transmitted light is yellow.

$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ absorbs in the yellow region of the spectrum, and the transmitted light is violet.



If we measure the wavelength, λ , of the photon absorbed, we can then calculate the splitting energy, $\Delta_o = hc/\lambda$. Stronger field ligands increase the magnitude of Δ_o therefore, shorter wavelengths of light are absorbed and longer wavelengths are transmitted.

PRACTICE Example: The color of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is light pink, whereas that of tetrahedral $[\text{CoCl}_4]^{2-}$ is deep blue. Explain this difference in color.

❖ Rules of Color Intensity and Forbidden Transitions

- The intensity of the transmitted color is based on two rules:
 - (1) If there is a center of symmetry in the molecule (i.e. center of inversion) then a **g to g** or **u to u** electron excitation is **not allowed**. **Spectroscopic selection rules** say that *transitions between states of the same parity are strictly forbidden; the Laporte rule*.
 - (2) **Spin multiplicity**: the **spin multiplicity of a complex cannot change** when an electron is excited. Multiplicity can be calculated via the equation **2S+1** where S is calculated by $(1/2)(\text{number of unpaired d-electrons})$. *Allowed transitions occur between states of the same multiplicity, say, singlet to singlet or triplet to triplet.*

If a complex breaks one of these rules, we say **it is a forbidden transition**. If one rule is broken, it is *singly forbidden*. If two rules are broken, we call it *doubly forbidden* and so on. Even though the convention is to call it forbidden, this does not mean it will not happen; rather, the more rules the complex breaks, the more faded its color will be because the more unlikely the chances the transition will happen. Let's again look at the example (Figure 22.19)

If we apply the intensity rules to it:

- (1) If we assume this molecule is octahedral in symmetry, this means it has an inversion center and thus the transition of e_g^* to t_{2g} is forbidden under rule 2 due to both orbitals being gerade (g).
- (2) Multiplicity before transition = $2[0.5(1 \text{ unpaired electron})] + 1 = 3$, Multiplicity after transition = $2[0.5(1 \text{ unpaired electron})] + 1 = 3$. Both multiplicities are the same, so this transition is allowed under rule 1.

Based on these rules, we can see that this transition is only singly forbidden, and thus it will appear only slightly faded and light rather than a deep, rich green.

- The **Laporte selection rule** for centrosymmetric molecules (those with a center of inversion) and atoms states that: The only ***allowed transitions are transitions that are accompanied by a change of parity***. That is, $u \rightarrow g$ and $g \rightarrow u$ transitions are allowed, but $g \rightarrow g$ and $u \rightarrow u$ transitions are **forbidden**.
- ✓ According to the Laporte rule, d-d transitions are ***parity-forbidden in octahedral complexes*** because they are $g \rightarrow g$ transitions ($e_g - t_{2g}$ transitions). *If the ligand environment is not strictly octahedral* (e.g., because of a slight static distortion), then the ***center of symmetry of the complex as a whole may be lost***, and with it the definitive even parity of the d orbitals and states. The fact that these ***d → d bands, though rather weak, are indeed observed*** is due to the loss of parity which can arise as vibronic transitions as a result of coupling to asymmetrical vibrations such as that shown in Fig. 11.7 (in either a static or a dynamic manner).
- ✓ A $d \rightarrow d$ transition may then become weakly allowed, frequently because the lowered symmetry allows p and d orbitals to mix. This is particularly true of ***tetrahedral complexes***. ***The tetrahedron has no center of symmetry and the d → d transitions of tetrahedral complexes are invariably more intense than those of their octahedral counterparts.***
- ✓ Further, allowed transitions occur between states of the same multiplicity, say, singlet to singlet or triplet to triplet. ***d → d transitions which involve a change of multiplicity, say, triplet to singlet, are doubly forbidden*** and are very weak indeed. But as ***spin-orbit coupling grows*** in the 4d and 5d series of metals, and especially in the rare earths, nominally spin-forbidden transitions gain in intensity because of the loss of a clearly defined multiplicity for each state.

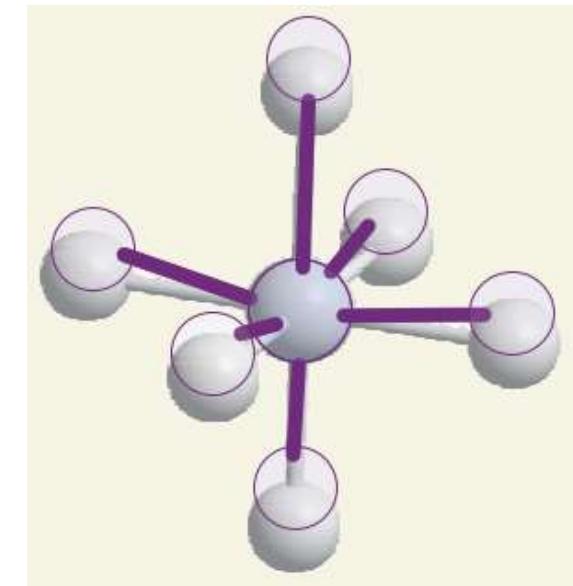


Fig. 11.7 A d-d transition is parity-forbidden because it corresponds to a g-g transition. However, a vibration of the molecule can destroy the inversion symmetry of the molecule and the g,u classification no longer applies. The removal of the centre of symmetry gives rise to a vibronically allowed transition.

- One can thus only expect absorption or emission of light by molecules that possess a dipole momentum. Typically, these will be permanent dipoles, but in some applications dipoles may also be induced in molecules that have no permanent dipole momentum.
- *Chromophores* are the light absorbing moieties within a molecule. Due to differences in electronegativity between individual atoms, they possess a spatial distribution of electric charge. This results in a dipole momentum $\bar{\mu}_0$ (ground state), such as for example the permanent dipole momentum of a carboxylic acid or an amide group.
- When light is absorbed by the chromophore, the distribution of electric charge is altered and the dipole momentum changes accordingly ($\vec{\mu}_1$; excited state). The transition dipole momentum $\vec{\mu}_{01}$ is the vector difference between the dipole momentum of the chromophore in the ground and the excited state. ***This transition dipole momentum is a measure for transition probability***, and its **dipole strength**, D_{01} , is defined as the squared length of the transition dipole momentum vector:
- $D_{01} = |\vec{\mu}_{01}|^2$
- The strength of this transition dipole momentum is directly related to the probability with which a transition occurs, i.e. the strength of an absorption band.
- Spectroscopic data can thus be analyzed to obtain numerical values for a transition dipole momentum which connects the absorption spectrum to the quantum mechanical wave function of a molecule.
- In **charge-transfer transitions** the ***electron moves through a considerable distance*** (the transfer of an electron from the ligands into the d orbitals of the central atom, or vice versa), which means that the ***transition dipole moment may be large and the absorption is correspondingly intense***.
- The intensities of charge-transfer transitions are proportional to the square of the transition dipole moment, in the usual way. We can think of the transition moment as a measure of the distance moved by the electron as it migrates from metal to ligand or vice versa, with a large distance of migration corresponding to a large transition dipole moment and therefore a high intensity of absorption.

❖ Charge-Transfer Color

The CF model is concerned solely with the energies of the d-electron states but the intense colors of many transition-metal complexes, e.g., the purple color of $[\text{MnO}_4]^-$ and the blood red of $[\text{Fe}(\text{CNS})_6]^{3-}$, arise **not from** $\text{d} \rightarrow \text{d}$ transitions, which as we have seen above are normally very weak, but from ***charge-transfer transitions in which electrons are transferred from the ligands to the metal (LMCT)***.

$[\text{Fe}(2,2'\text{-bipyridine})_3]^{2+}$ shows a strong absorption at 522 nm due to the reverse process, a ***metal-to-ligand charge transfer (MLCT)***.

Transitions of this type are further evidence of covalency and require a molecular orbital treatment for their quantitative understanding.



KMnO_4



K_2CrO_4



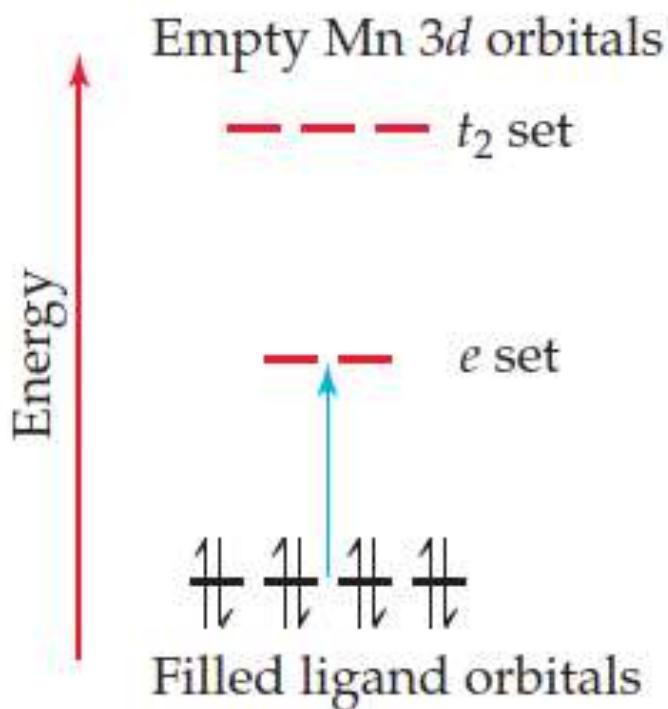
KClO_4

Figure 23.35 The colors of compounds can arise from charge-transfer transitions. KMnO_4 and K_2CrO_4 are colored due to ligand-to-metal charge-transfer transitions in their anions. Higher energy ultraviolet photons are needed to excite the charge-transfer transition in the perchlorate ion, therefore KClO_4 is white.

- You have probably seen many colorful transition-metal compounds, including those shown in Figure 23.35. Many of these compounds are colored because of d-d transitions.
- Some colored complexes, however, including the violet permanganate ion, MnO_4^- , and the yellow chromate ion, CrO_4^{2-} , derive their **color from a different type of excitation involving the d orbitals**.
- A complex may absorb radiation as a result of the ***transfer of an electron from the ligands into the d orbitals of the central atom, or vice versa***. This mode of chromophore activity is shown by the permanganate ion, MnO_4^- , and accounts for its intense violet color. In this oxoanion, the electron migrates from an orbital that is largely confined to the O atom ligands to an orbital that is largely confined to the Mn atom. It is therefore an example of a **ligand-to-metal charge-transfer transition (LMCT)**.
- The reverse migration, a **metal-to-ligand charge-transfer transition (MLCT)**, can also occur. An example is the transfer of a d electron into the antibonding π orbitals of an aromatic ligand. The resulting excited state may have a very long lifetime if the electron is extensively delocalized over several aromatic rings, and such species can participate in photochemically induced redox reactions.

- The permanganate ion strongly absorbs visible light (which arises from strong absorption within the range of 420–700 nm), with maximum absorption at 565 nm. Because violet is complementary to yellow, this strong absorption in the yellow portion of the visible spectrum is responsible for the violet color of salts and solutions of the ion.
- ✓ What is happening during this absorption of light?
- ✓ The MnO_4^- ion is a complex of Mn(VII). Because **Mn(VII)** has a $[\text{Ar}]3\text{d}^0$ electron configuration, ***the absorption cannot be due to a d-d transition because there are no d electrons to excite!***
- ✓ That does not mean, however, that the d orbitals are not involved in the transition. The excitation in the MnO_4^- ion is due to a **charge-transfer transition, in which an electron on one oxygen ligand is excited into a vacant d orbital on the Mn ion** (Figure 23.36).
- ✓ In essence, an electron is transferred from a ligand to the metal, so this transition is called a **ligand-to-metal charge-transfer (LMCT) transition**.
- ✓ An LMCT transition is also responsible for the color of the CrO_4^{2-} , which contains the Cr(VI) ion with an $[\text{Ar}]3\text{d}^0$ electron configuration.

Figure 23.36 Ligand-to-metal charge-transfer transition in MnO_4^- . As shown by the blue arrow, an electron is excited from a nonbonding orbital on O into one of the empty d orbitals on Mn.



- A salt of the perchlorate ion (ClO_4^-) appears colorless (as shown in Figure 23.35). Like MnO_4^- , ClO_4^- is tetrahedral and has its central atom in the +7 oxidation state. However, because the Cl atom ***does not have low-lying d orbitals***, exciting an electron from O to Cl ***requires a more energetic photon*** than does it does in MnO_4^- . The first absorption for ClO_4^- is in the ***ultraviolet portion*** of the spectrum, so no visible light is absorbed and the salt appears white.

- Other complexes exhibit charge-transfer excitations in which an electron from the metal atom is excited to an empty orbital on a ligand. Such an excitation is called a **metal-to-ligand charge-transfer (MLCT)** transition.
- Lastly, **metal-to-metal charge-transfer (MMCT)** bands occur between metal-centered orbitals on two different metals within the same complex, such as those in Prussian blue. In the case of mixed-valence compounds, *one of the metals must be in a low oxidation state so that it can act as an electron donor, while the other metal exists in a high oxidation state and acts as the electron acceptor.*
- ✓ Prussian blue is a coordination compound containing both iron(II) and iron(III) linked together by cyanide ligands ($\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$).
- ***Charge-transfer transitions are generally more intense than d-d transitions.***
- Many metal-containing pigments used for oil painting, such as cadmium yellow (CdS), chrome yellow (PbCrO_4), and red ochre (Fe_2O_3), have intense colors because of ***charge-transfer transitions.***

Tetragonally distorted complexes: Jahn–Teller effect or Jahn–Teller distortion

Key points: A tetragonal distortion can be expected when the ground electronic configuration of a complex is **orbitally degenerate** and **asymmetrically filled**; the complex will distort so as to remove the degeneracy and achieve lower energy.

- Six-coordinate ***d*⁹ complexes of copper(II)** usually depart considerably from octahedral geometry and show pronounced tetragonal distortions (Fig. 20.11).
- High-spin *d*⁴ (for instance, Cr²⁺ and Mn³⁺) and low-spin *d*⁷ six-coordinate complexes (for instance, Ni³⁺) may show a similar distortion, but *complexes of these ions are less common*, and the distortions are less pronounced than those in copper(II)).

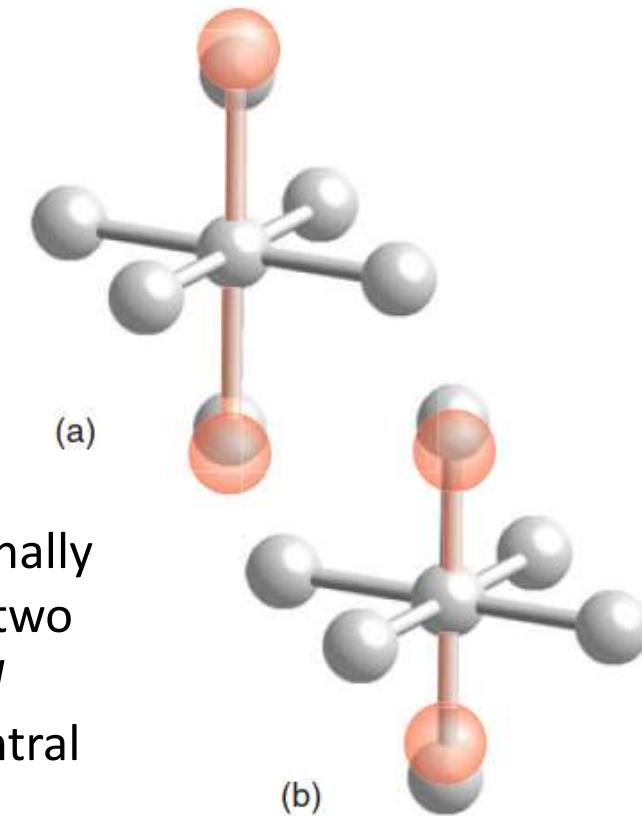


Figure 20.11 (a) A tetragonally distorted complex where two of the ligands have *moved further away* from the central ion.
(b) A tetragonally distorted complex where two of the ligands have *moved closer* towards the central ion.

- The Jahn-Teller effect is a geometric distortion of a non-linear molecular system that reduces its symmetry and energy.
 - This distortion is typically observed among octahedral complexes where the two axial bonds can be shorter or longer than those of the equatorial bonds. This effect can also be observed in tetrahedral compounds. This effect is dependent on the electronic state of the system.
 - In 1937, Hermann Jahn and Edward Teller postulated a theorem stating that "stability and degeneracy are not possible simultaneously unless the molecule is a linear one," in regard to its electronic state. This leads to a break in degeneracy which stabilizes the molecule and by consequence, reduces its symmetry. Since 1937, the theorem has been revised which Housecroft and Sharpe have eloquently phrased as "any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy." This is most commonly observed with transition metal octahedral complexes, however, it can be observed in tetrahedral compounds as well.
 - For a given octahedral complex, the five d atomic orbitals are split into two degenerate sets when constructing a molecular orbital diagram. These are represented by the sets' symmetry labels: t_{2g} (d_{xz} , d_{yz} , d_{xy}) and e_g (d_{z^2} and $d_{x^2-y^2}$). When a molecule possesses a degenerate electronic ground state, it will distort to remove the degeneracy and form a lower energy (and by consequence, lower symmetry) system. The octahedral complex will either elongate or compress the z ligand bonds as shown in Figure 8.2.2.1.1 below:
 - When an octahedral complex exhibits elongation, the axial bonds are longer than the equatorial bonds. For a compression, it is the reverse; the equatorial bonds are longer than the axial bonds. Elongation and compression effects are dictated by the amount of overlap between the metal and ligand orbitals. Thus, this distortion varies greatly depending on the type of metal and ligands. In general, the stronger the metal-ligand orbital interactions are, the greater the chance for a Jahn-Teller effect to be observed.

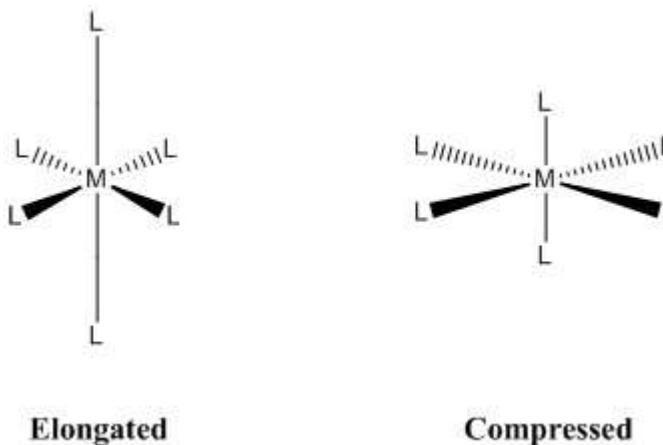


Figure 8.2.2.1.1: Jahn-Teller distortions for an octahedral complex.

- These distortions are manifestations of the **Jahn–Teller effect**: if the ground electronic configuration of a **nonlinear** complex is **orbitally degenerate** and **asymmetrically filled**, then the complex distorts so as to remove the degeneracy and achieve a lower energy.

➤ The physical origin of the effect is quite easy to identify. Thus, a *tetragonal distortion of a regular octahedron*, corresponding to extension along the z-axis and compression on the x- and y-axes, lowers the energy of the $e_g(d_{z^2})$ orbital and increases the energy of the $e_g(d_{x^2-y^2})$ orbital (Fig. 20.12).

➤ For example, in a d^9 complex (with a configuration that would be $t_{2g}^6 e_g^3$ in O_h), such a distortion leaves two electrons in the d_{z^2} orbital with a lower energy and one in the $d_{x^2-y^2}$ orbital with a higher energy.

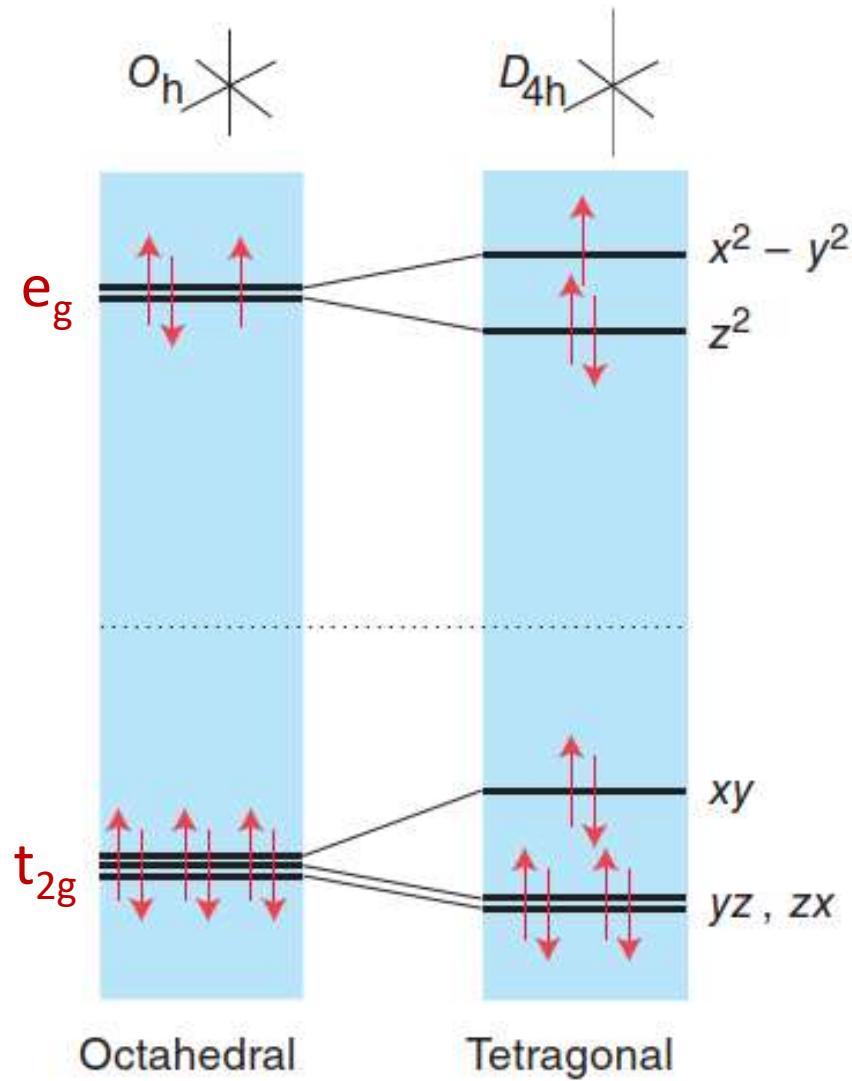
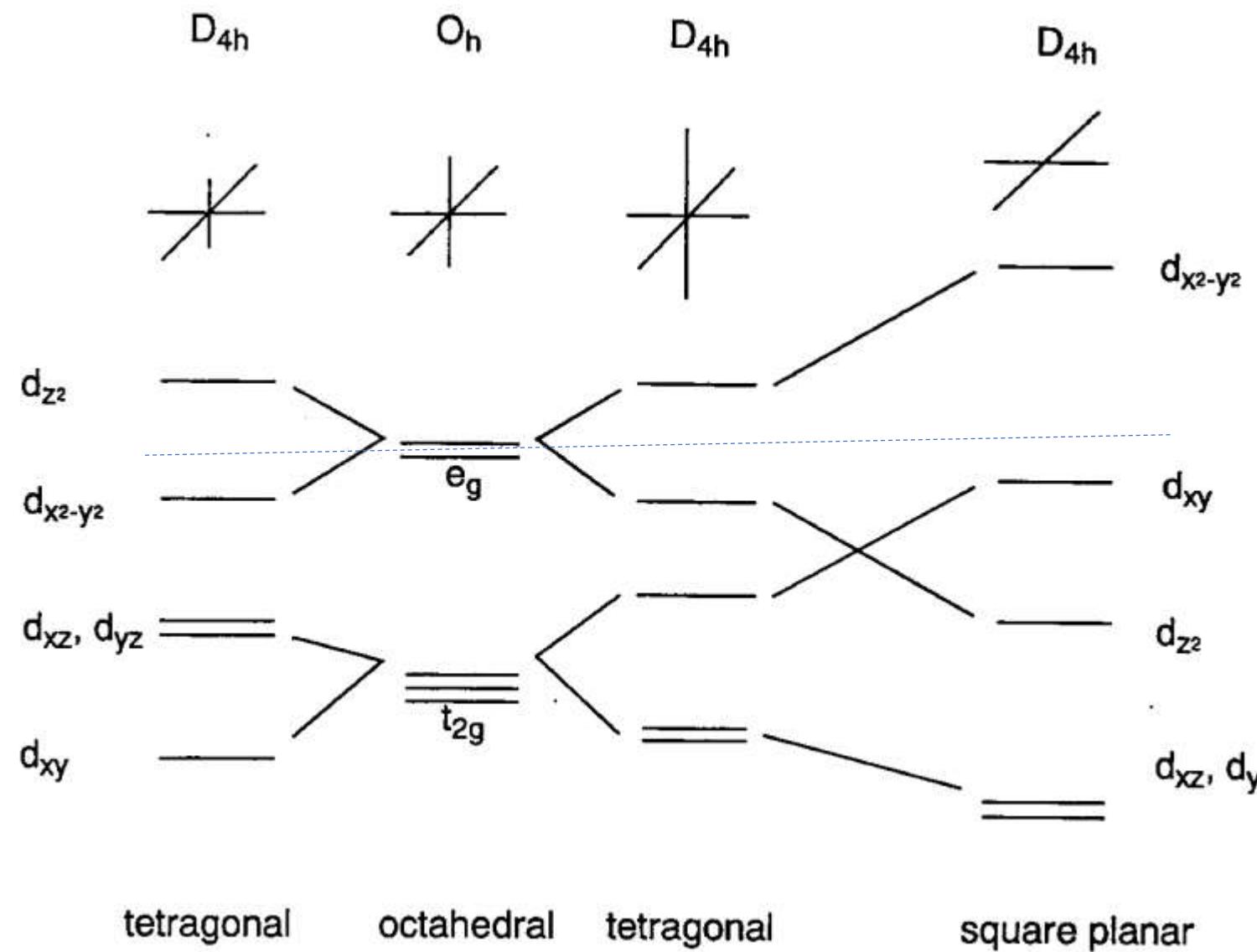


Figure 20.12 The effect of tetragonal distortions (compression along x and y and extension along z) on the energies of d orbitals. The orbital occupation is for a d^9 complex.

- They have a d⁹ configurations and the e_g orbitals in the octahedral structure are occupied by three electrons.
- ✓ If the e_g orbitals split and two electrons occupy the lower orbital and one electron the upper orbital, **the system gains energy of a half of the energy difference, δ , of two split orbitals**. Therefore, a tetragonal distortion in the z axis becomes favorable with respect to Octahedral.
- ✓ Therefore, if **one** or **three electrons occupy the e_g orbitals (as in high-spin d⁴, low-spin d⁷, and d⁹ complexes)** a **tetragonal distortion may be energetically advantageous**.

Figure 6.2.7: Change of the orbital energy from octahedral to square planar complexes.



Elongation

- Elongation Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals with a z component, while the orbitals without a z component are destabilized (higher in energy) as shown in Figure 8.2.2.1.2 below:
- This is due to the d_{xy} and $d_{x^2-y^2}$ orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the $d_{x^2-y^2}$ orbital is antibonding, it is expected to increase in energy due to elongation. The d_{xy} orbital is still nonbonding but is destabilized due to the interactions.
- When the octahedral complex undergoes an elongation, any of the metal d orbitals that carry a z-directional feature become lower in energy, ligands are easier to bond along z-direction. Geometrically, as the z-direction gets elongated, the repulsion energy and sterical hindrance along z-direction are lower to allow ligands easier to bond.

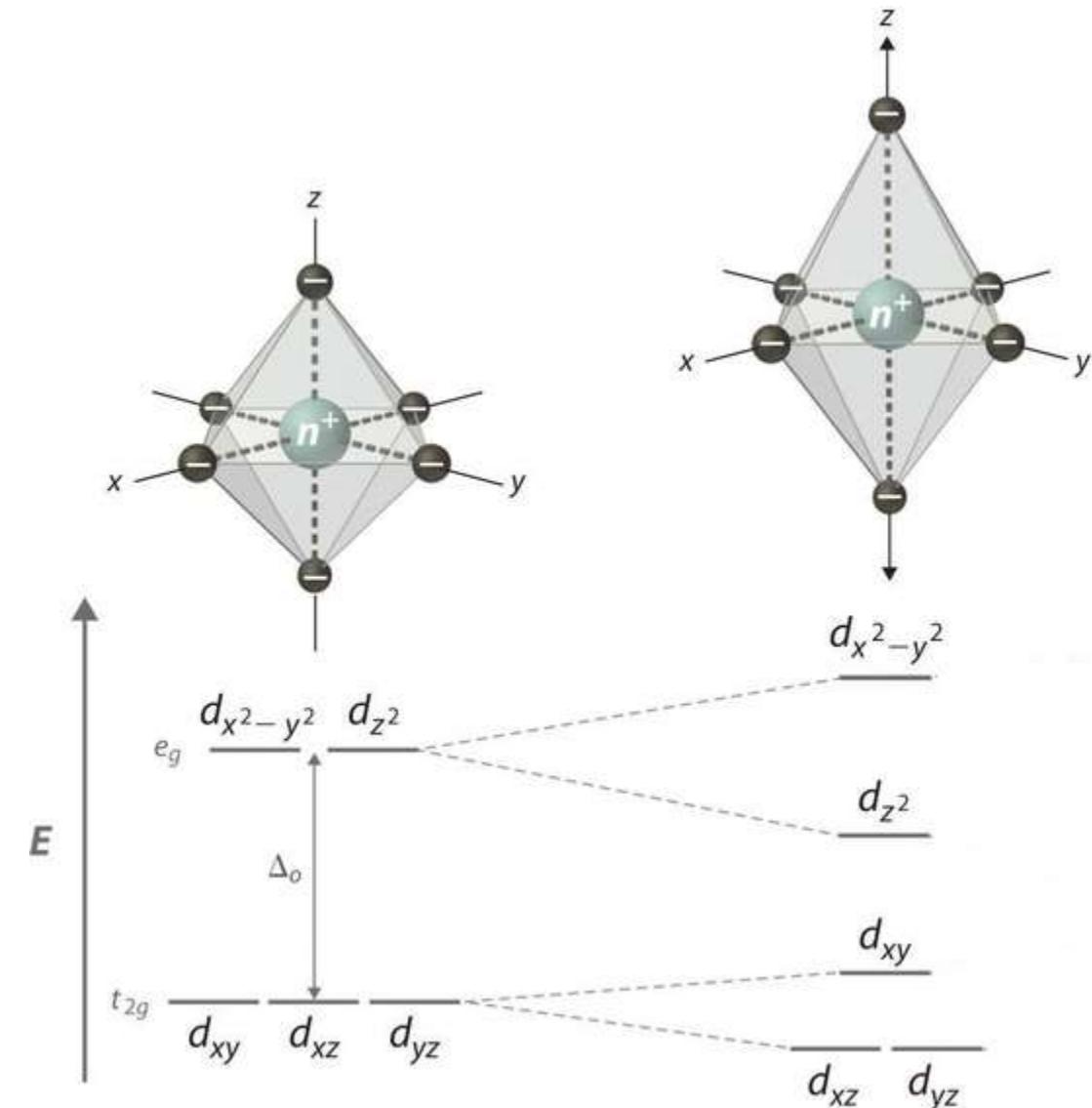


Figure 8.2.2.1.2: Illustration of tetragonal distortion (elongation) for an octahedral complex.

➤ Jahn-Teller elongations are well-documented for copper(II) octahedral compounds. A classic example is that of copper(II) fluoride as shown in Figure 8.2.2.1.3.

➤ Notice that the two axial bonds are both elongated and the four shorter equatorial bonds are the same length as each other. According to the theorem, the orbital degeneracy is eliminated by distortion, making the molecule more stable based on the model presented in Figure 8.2.2.1.2.

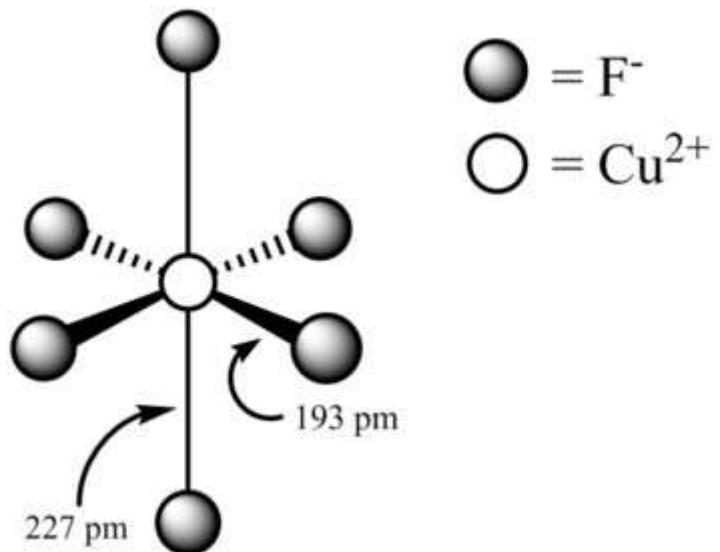


Figure 8.2.2.1.3: Structure of octahedral copper(II) fluoride.

Compression

➤ Compression Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals without a z component, while the orbitals with a z component are destabilized (higher in energy) as shown in Figure 8.2.2.1.4 below:

- This is due to the z-component d orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the d_{z^2} orbital is antibonding, it is expected to increase in energy due to compression. The d_{xz} and d_{yz} orbitals are still nonbonding but are destabilized due to the interactions.
- When the octahedral complex undergoes a compression, any of the metal d orbitals that carry a z-directional feature become higher in energy, ligands are harder to bond along z-direction. Geometrically, as the z-direction gets compressed, the repulsion energy and steric hindrance along z-direction are higher, which makes ligands more difficult to bond.

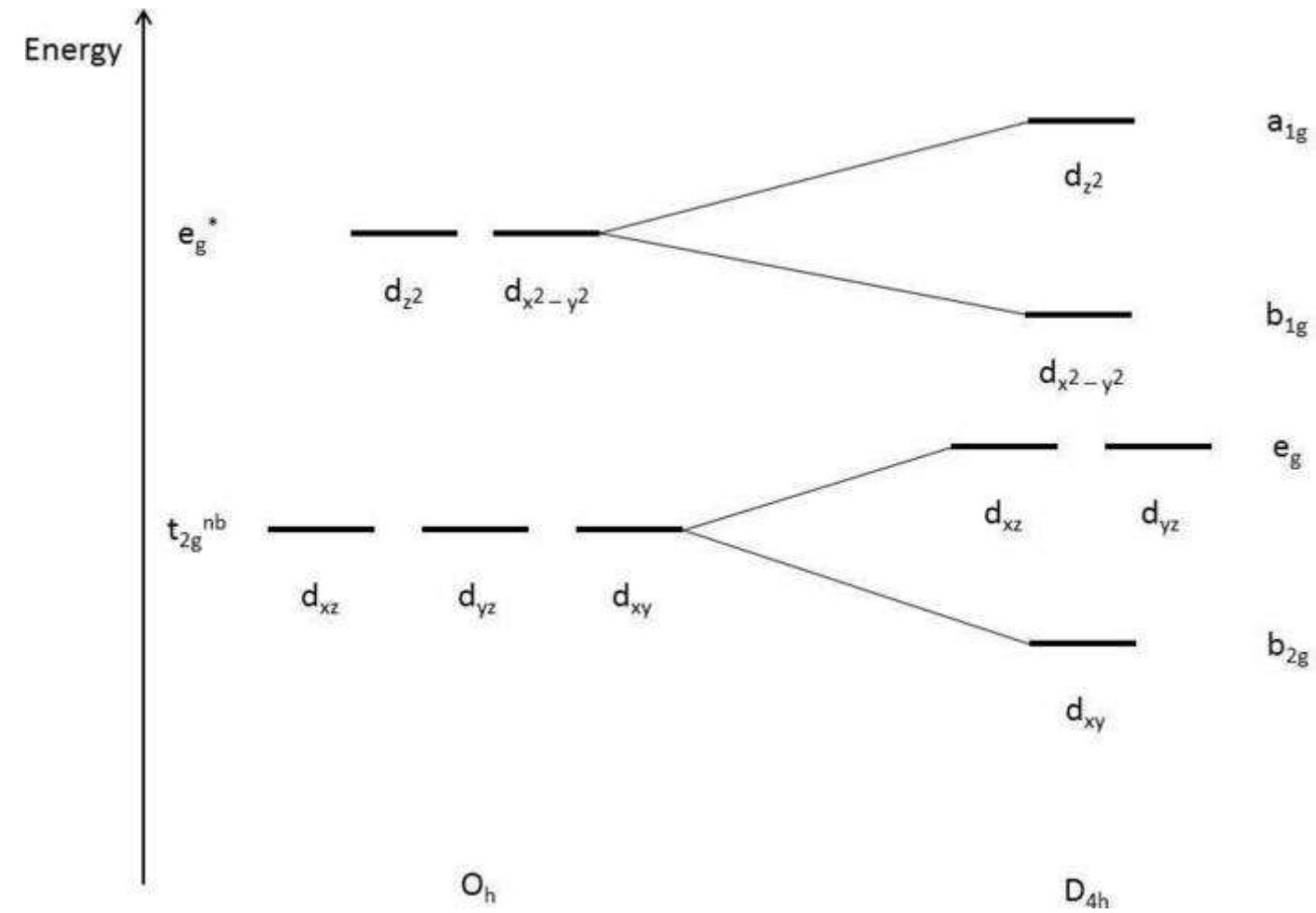


Figure 8.2.2.1.4: Illustration of tetragonal distortion (compression) for an octahedral complex.
e.g. KCrF_3 (as $[\text{CrF}_6]^{4-}$): 4 F at 214 pm 2 F at 200 pm.

d-orbitals and their associated Jahn-Teller Distortion: Electronic Configurations

- For Jahn-Teller effects to occur in transition metals there must be degeneracy in either the t_{2g} or e_g orbitals. The electronic states of octahedral complexes depend on the number of d-electrons and the splitting energy, Δ . When Δ is large and is greater than the energy required to pair electrons, electrons pair in t_{2g} before occupying e_g . On the other hand, when Δ is small and is less than the pairing energy, electrons will occupy e_g before pairing in t_{2g} . The Δ of an octahedral complex is dictated by the chemical environment (ligand identity), and the identity and charge of the metal ion. If the electron configurations for any d-electron count is different depending on Δ , the configuration with more paired electrons is called low spin while the one with more unpaired electrons is called high spin.
- The electron configurations diagrams for d1 through d10 with large and small Δ are illustrated in the figures below. Notice that the electron configurations for d^1 , d^2 , d^3 , d^8 , d^9 , and d^{10} are the same no matter what the magnitude of Δ . Low spin and high spin configurations exist only for the electron counts d^4 , d^5 , d^6 , and d^7 .

□ Which d^n electron configurations would show a Jahn–Teller effect?

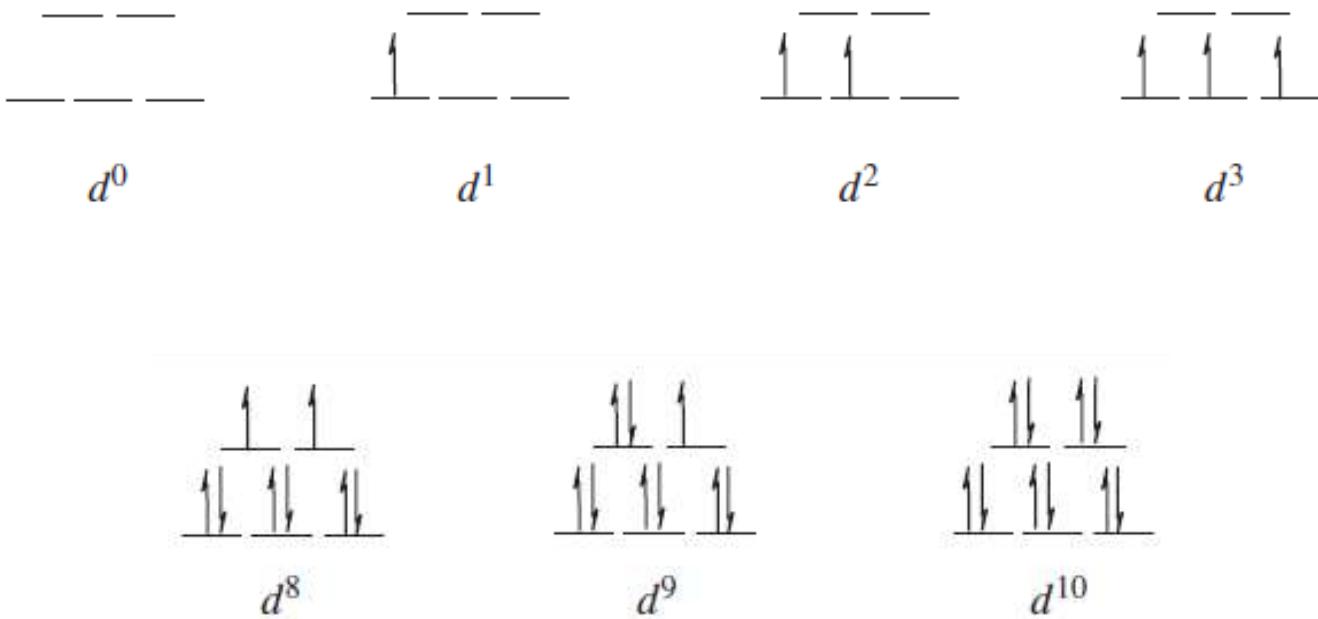
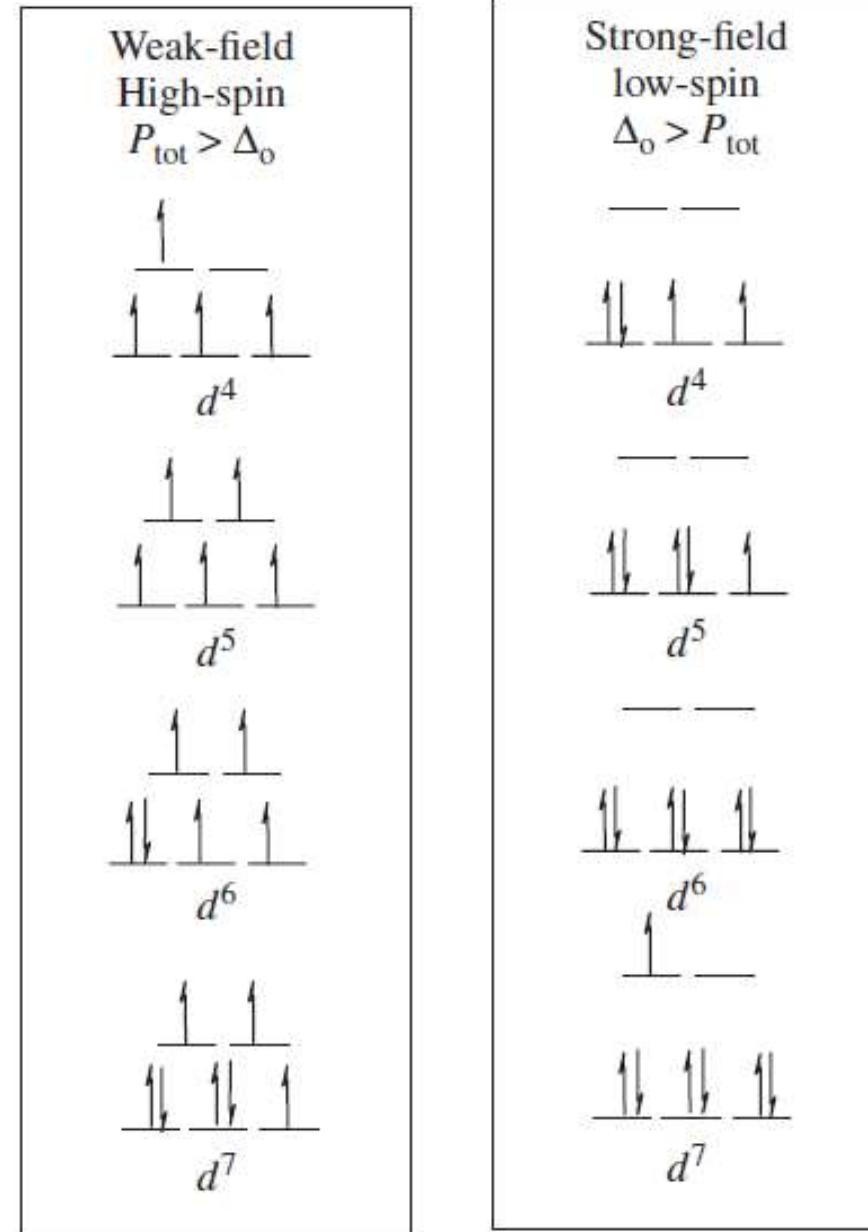


FIGURE.....

Crystal field splitting diagram for the different d^n configurations in an **octahedral CF**



□ Which d^n electron configurations would show a Jahn–Teller effect?

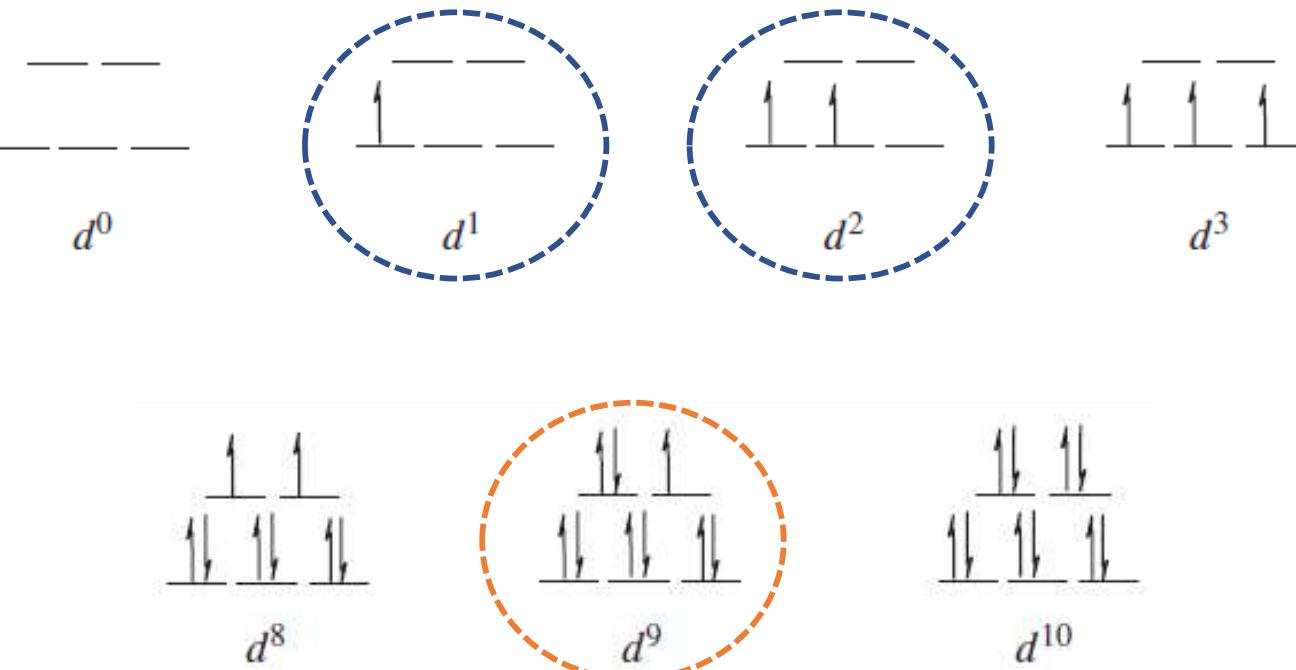
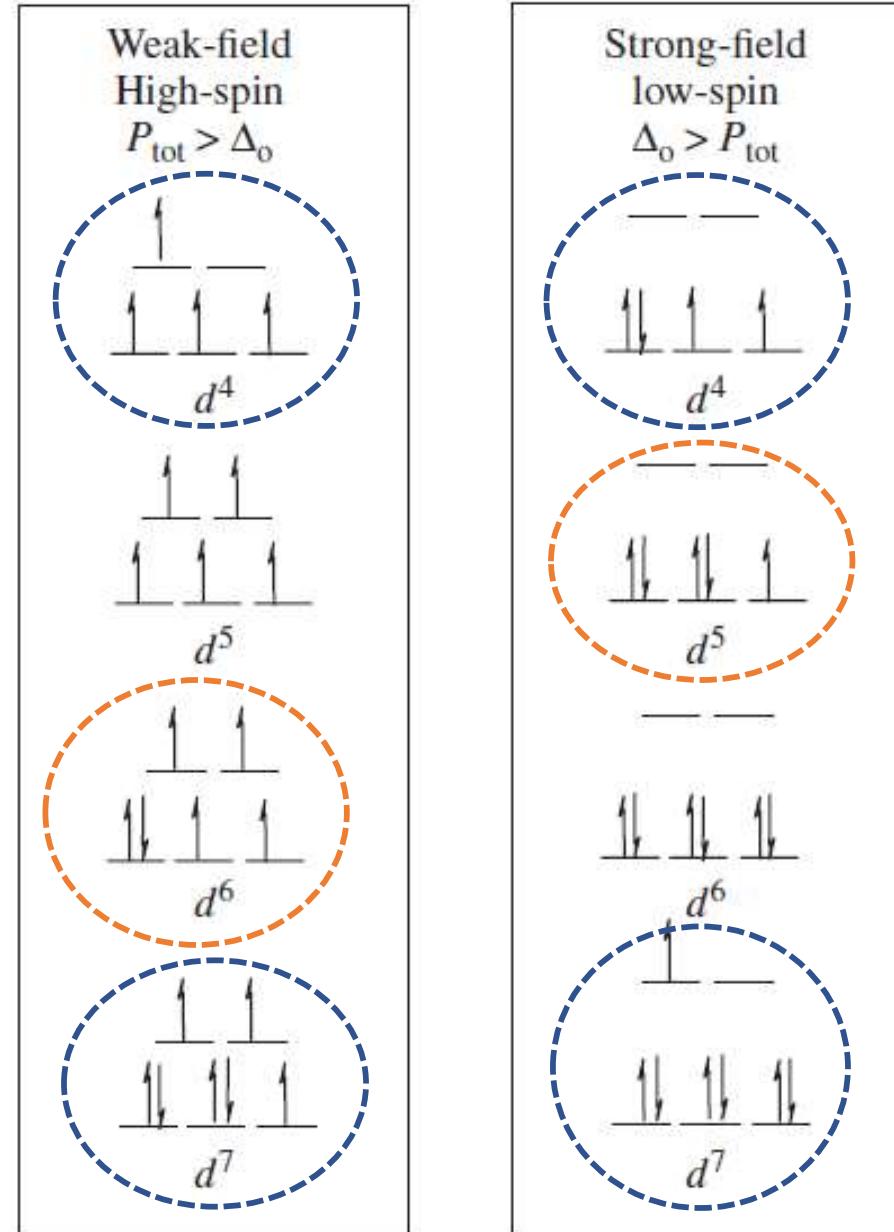


FIGURE.....

Crystal field splitting diagram for the different d^n configurations in an octahedral CF.



Which d^n electron configurations would show a Jahn–Teller effect?

Number of <i>d</i> electrons	<i>Electronic configuration</i>	
	<i>e</i>	<i>t</i> ₂
1	↑	
2	↑	↑
3	↑	↑
4	↑	↑
5	↑	↑
6	↑↓	↑
7	↑↓	↑↓
8	↑↓	↑↓
9	↑↓	↑↓
10	↑↓	↑↓

FIGURE.....

Crystal field splitting diagram for the different d^n configurations in a **tetrahedral** CF.

Which d^n electron configurations would show a Jahn–Teller effect?

Number of d electrons	Electronic configuration		
	e	t_2	
1	↑		
2	↑	↑	
3	↑	↑	
4	↑	↑	
5	↑	↑	
6	↑↓	↑	
7	↑↓	↑↓	
8	↑↓	↑↓	
9	↑↓	↑↓	
10	↑↓	↑↓	

FIGURE.....

Crystal field splitting diagram for the different d^n configurations in a **tetrahedral CF**.

❖ Two Types of Distortions:

- The Jahn–Teller effect identifies an unstable geometry (**a nonlinear complex with an orbitally degenerate ground state**); however, *it does not predict the preferred distortion.*
- For instance, with an octahedral complex, *instead of axial elongation and equatorial compression*, the degeneracy can **also** be removed by axial compression and equatorial elongation.
- Which distortion (elongation or compression) occurs in practice is **a matter of energetics**, not symmetry.
- However, because *axial elongation weakens two bonds, but equatorial elongation weakens four*, *axial elongation is more common than axial compression.*

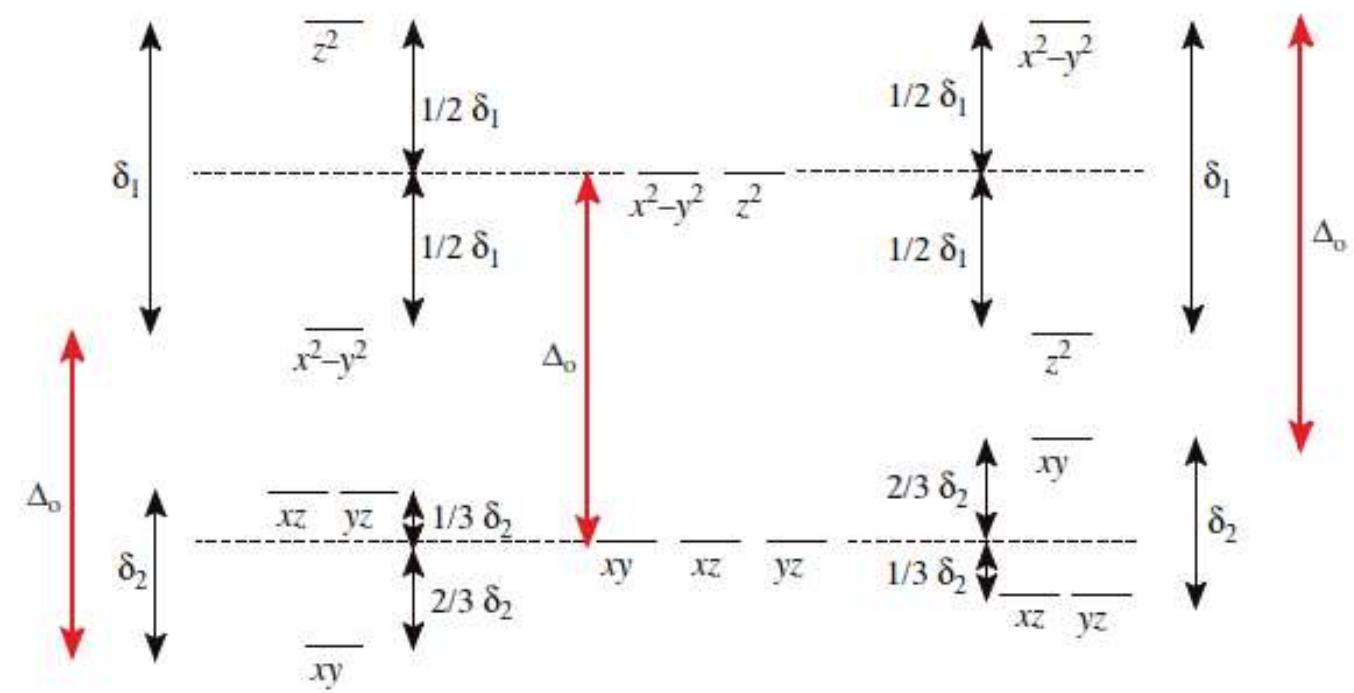
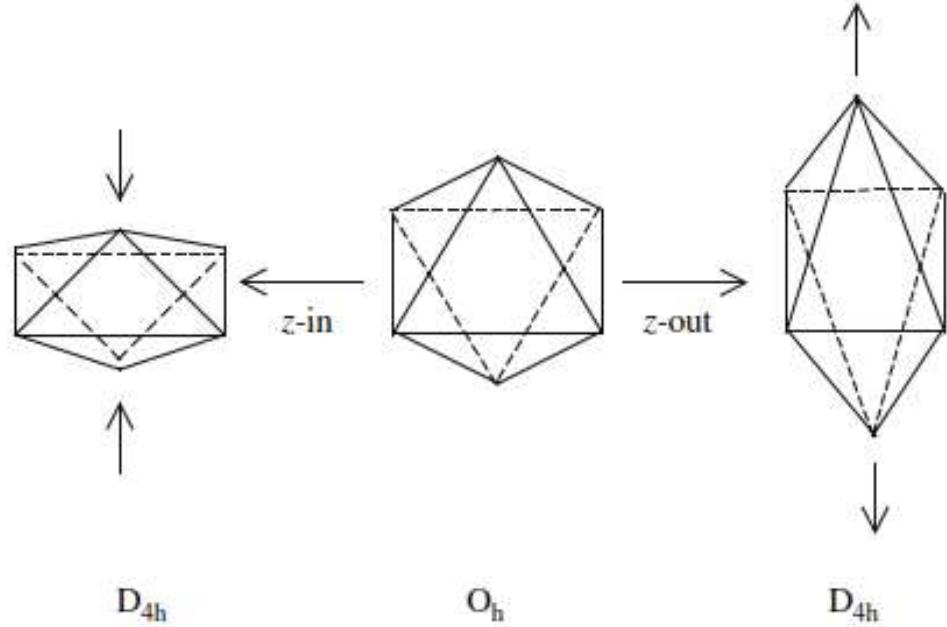
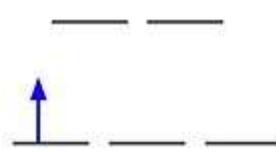
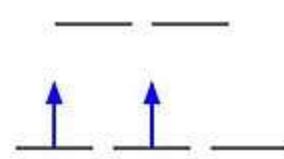


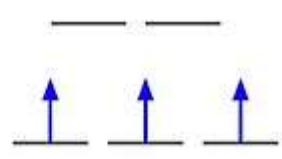
FIGURE 16.50 Tetragonal distortions from O_h symmetry and their effects on the energies of the d-orbitals. The “z-out” tetragonal distortion is shown on the right and the “z-in” tetragonal distortion is shown on the left.



d¹
(Compression)



d²
(Elongation)



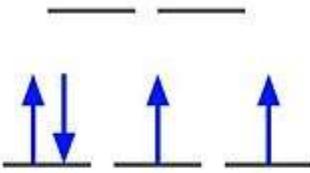
d³
(No Jahn-Teller Distortion)

d¹: **Compression** geometry gives $-(2/3)\delta_2$ stability.

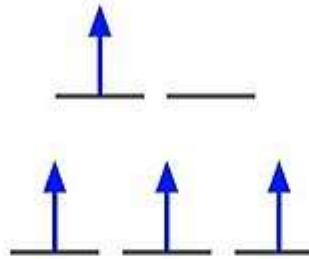
d¹: Elongation geometry gives $-(1/3)\delta_2$ stability.

d²: Compression geometry gives $[-(2/3)\delta_2 + P \text{ (Pairing)}]$ stability.

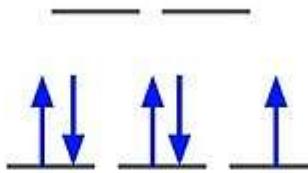
d²: **Elongation** geometry gives $[-2 \times (1/3)\delta_2] = -(2/3)\delta_2$ stability



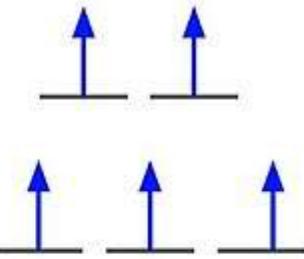
d⁴ Low-spin
(Compression)



d⁴ High-spin
(Must distort but cannot specify whether it is elongated or compressed.)



d⁵ Low-spin
(Elongation)

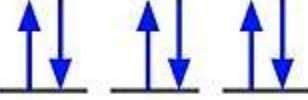
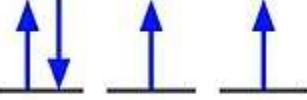
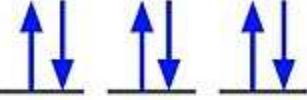
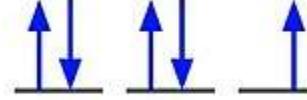


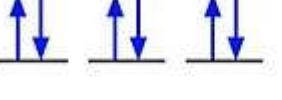
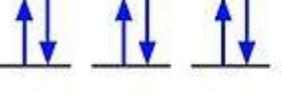
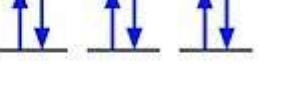
d⁵ High-spin
(No Jahn-Teller Distortion)

d⁴ Low-Spin: **Compression** geometry gives $(xy)^2(xz)^1(yz)^1$ which gives $[-2 \times (2/3)\delta_2 + 2 \times (1/3)\delta_2] = -(2/3)\delta_2$ stability. **No P (Pairing)** energy cost, because already there was one pair in the low-spin d⁴ system. Therefore, no change in pairing number.

d⁴ Low-Spin: Elongation geometry gives $(xz)^2(yz)^1(xy)^1$ which gives $[-3 \times (1/3)\delta_2 + 1 \times (2/3)\delta_2] = (1/3)\delta_2$ stability. **No P (Pairing)** energy cost, because already there was one pair in the low-spin d⁴ system.

Therefore, no change in pairing number.

			
d⁶ Low-spin (No Jahn-Teller Distortion)	d⁶ High-spin (Compression)	d⁷ Low-spin (Must distort but cannot specify whether it is elongated or compressed.)	d⁷ High-spin (Elongation)

		
d⁸ (No Jahn-Teller Distortion)	d⁹ (Must distort but cannot specify whether it is elongated or compressed.)	d¹⁰ (No Jahn-Teller Distortion)

❖ The Strength of Jahn-Teller Distortion

General Strength Trend of Jahn-Teller Distortion

For octahedral complexes:

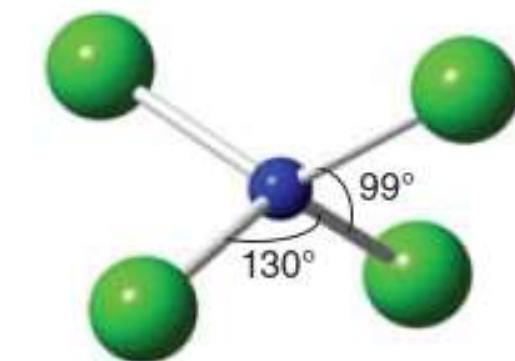
- **weak** Jahn-Teller effect if t_{2g} is unevenly occupied
- **strong** Jahn-Teller effect if e_g is **unevenly** occupied

Table of Jahn-Teller Distortion Strength

Number of d-electrons	1	2	3	4	5	6	7	8	9	10
High-spin	w	w	-	s	-	w	w	-	s	-
Low-spin	w	w	-	w	w	-	s	-	s	-

The table of d-orbitals Jahn-Teller distortion strength w = weak Jahn-Teller effect expected; s = strong Jahn-Teller effect expected;
- = no Jahn-Teller distortion

- A Jahn–Teller effect is possible for other electron configurations of octahedral complexes (the d^1 , d^2 , low-spin d^4 and d^5 , high-spin d^6 , and d^7 configurations) and for tetrahedral complexes (the d^1 , d^3 , d^4 , d^6 , d^8 , and d^9 configurations).
- However, as neither the t_{2g} orbitals in an octahedral complex nor any of the d orbitals in a tetrahedral complex point directly at the ligands, **the effect is normally much smaller**, as is any measurable distortion. Tetrahedral Cu^{2+} compounds often show a slightly ‘flattened’ tetrahedral geometry as seen for the $[\text{CuCl}_4]^{2-}$ anion in Cs_2CuCl_4 .



The flattened $[\text{CuCl}_4]^{2-}$ anion

- Various forms of ***experimental verification*** of the Jahn–Teller effect include the ***electronic spectra***, ***ESR spectra*** of coordination compounds, ***X-ray crystallographic data*** showing different M–L bond lengths, and ***thermodynamic*** data.
- ✓ As an example (of thermodynamic data), consider ***the stepwise formation constants*** in Table 16.28 for $[\text{Cu}(\text{NH}_3)_6]^{2+}$, which has the d⁹ electron configuration. As expected, the ***stability constants decrease with increasing n because there is less positive charge on the metal*** as it becomes more saturated with ligands. However, ***there is an abrupt drop in the stability of the Cu(II) compounds between n= 4 and n=5***. The reason that it is ***so difficult to add the fifth and sixth NH₃ ligands*** to Cu²⁺ is that the ***octahedral complex undergoes a “z-out” tetragonal distortion, which significantly weakens the two bonds along the z-axis***.

TABLE 16.28 Stepwise formation constants for $[\text{Cu}(\text{NH}_3)_n]^{2+}$.

K_1	2×10^4	K_4	2×10^2
K_2	4×10^3	K_5	3×10^{-1}
K_3	1×10^3	K_6	Very small

- A Jahn–Teller distortion can hop from one orientation to another and give rise to the dynamic Jahn–Teller effect. For example, below 20 K the EPR spectrum of $[\text{Cu}(\text{OH}_2)_6]^{2+}$ shows a static distortion (more precisely, one that is effectively stationary on the timescale of the resonance experiment). However, above 20 K the distortion disappears because it hops more rapidly than the timescale of the EPR observation.

❖ Jahn-Teller Distortion and Spectra: Spectra of the First-order Jahn-Teller Distortion

- In the first-order Jahn-Teller distortion, two electron transitions can be observed. This phenomenon can lead to a “double-hump” result on the absorption spectra as shown in Figure 1.17.5 and 1.17.6.

Figure 1.17.5: The absorption spectra of a first-order Jahn-Teller distortion

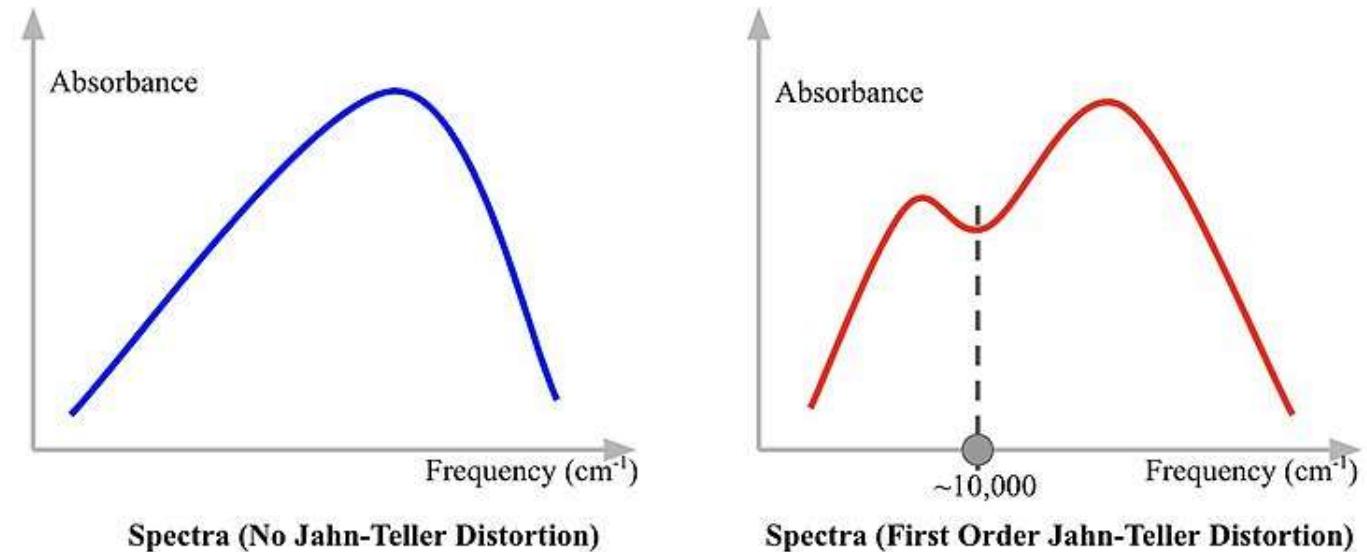
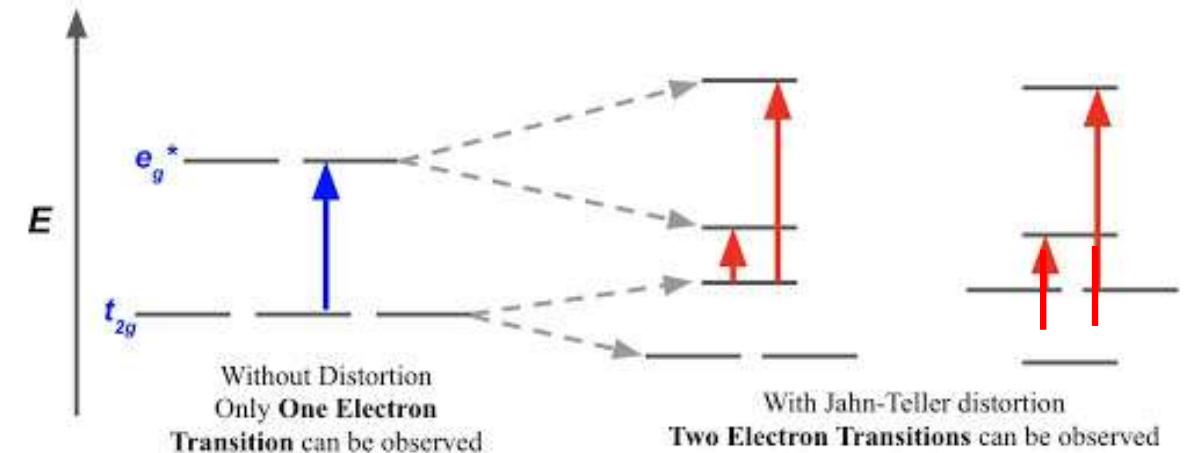


Figure 1.17.6: The electron transition in non-distorted (left) and distorted (right) orbitals



➤ Splitting of terms is observed in the ***electronic transitions*** of coordination compounds due to JT distortions. For instance, splitting of the terms for a d¹ [TiCl₆]³⁻ ion as it undergoes a tetragonal distortion from octahedral symmetry, illustrating the ***two observed spin-allowed transitions*** for the complex. The electronic spectrum of this d¹ coordination compound is ***expected*** to have ***a single LF transition*** in the absence of Jahn–Teller splitting. In fact, the spectrum of the [TiCl₆]³⁻ ion consists of ***two closely spaced peaks*** separated by approximately 1400cm⁻¹.

The Jahn-Teller Effect: An Example

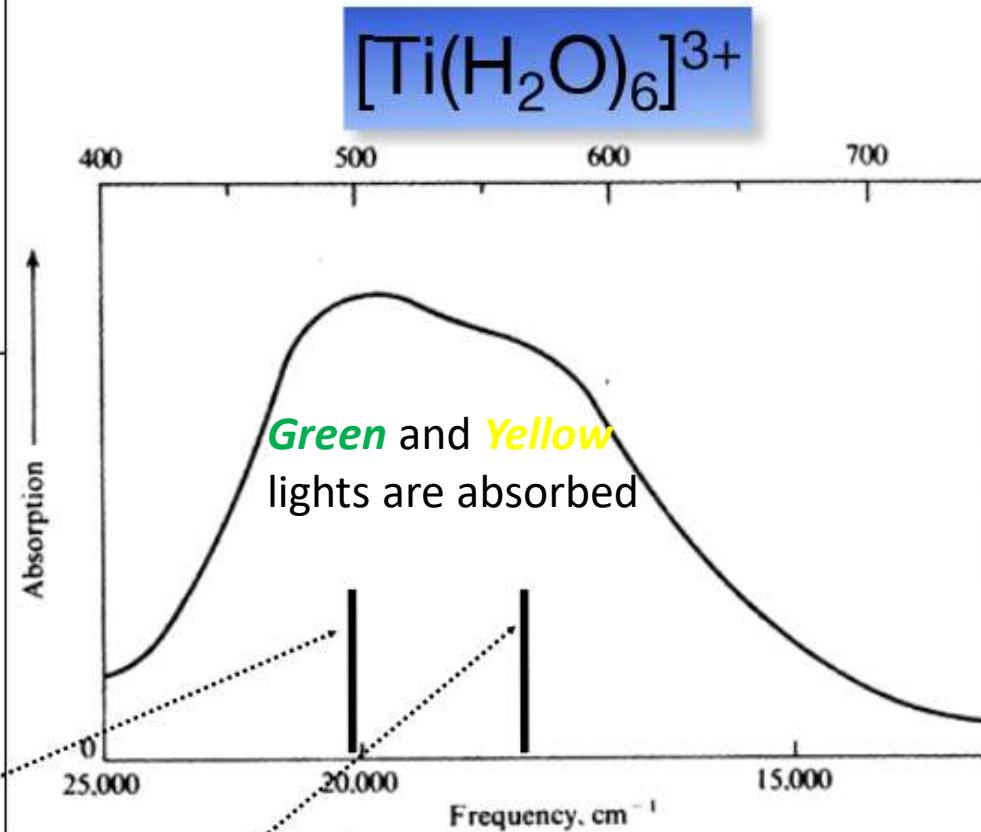
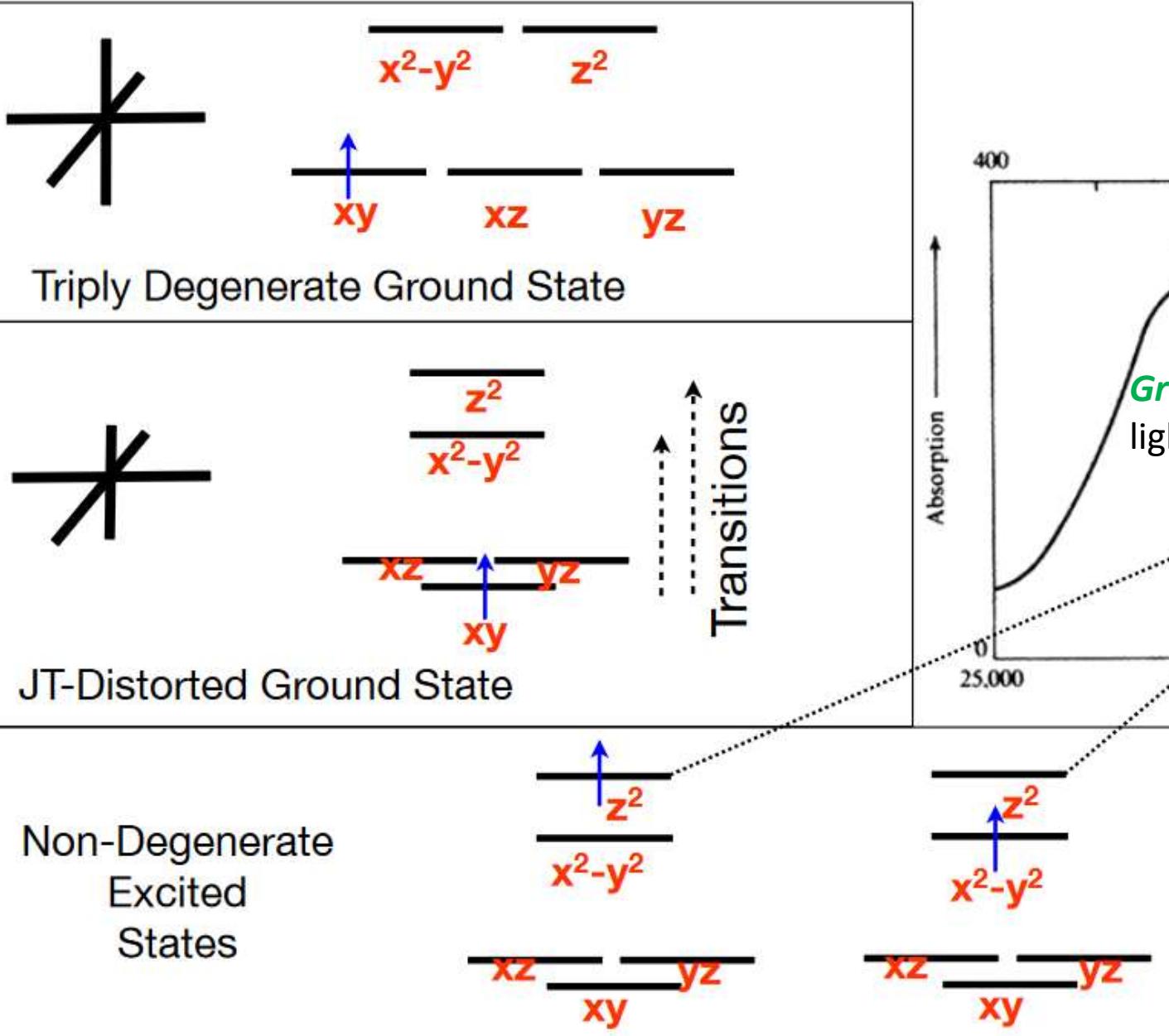


FIGURE 16.51. Splitting of the terms for a d¹ $[Ti(H_2O)_6]^{3+}$ ion as it undergoes a tetragonal distortion from octahedral symmetry, illustrating the two observed spin-allowed transitions for the complex. (Note: not drawn to scale.)

❖ The Second-order Jahn-Teller Distortion

- The *second order Jahn-Teller distortion occurs when the excited state of the transition metal has unequal occupation of d-orbitals with identical energies.*
- The ground state of the transition metal may not have unequal occupation of degenerate orbitals, therefore, the second order Jahn-Teller distortion is also called *Pseudo Jahn-Teller distortion*.

Ligand Field Theory: Why?

- Properties such as the absorption of visible light due to d-d-transitions and magnetic susceptibility of metal complexes can be macroscopically observed, and the crystal field theory delivers predictions that are in good agreement with macroscopic observations for some complexes.
- Crystal-field theory provides a simple conceptual model that can be used to interpret magnetic, spectroscopic, and thermochemical data by using empirical values of Δ_0 .
- Crystal field theory is based on a very primitive model of bonding. For example, *the theory treats ligands as point charges or dipoles, but ligands are not point charges*: they are actual molecules or ions.
- The theory ***does not take into account the overlap of ligand and metal-atom orbitals. It only considers the electrostatic interactions between metal and ligands and ignores any covalent character of metal-ligand bonds.***
- *You may have noticed that the ligand orbitals are not actually featured in the discussion. Further, the theory leaves several questions unanswered.*

- *The crystal-field theory **cannot account** for the ligand spectrochemical series.*
- Why, for instance, is the electrically neutral molecule CO a strong-field ligand but the negatively charged ion Cl⁻ a weak-field ligand?
- To improve the model of bonding in complexes, chemists have turned to *molecular orbital theory*.
- **Ligand field theory** describes bonding in complexes in terms of molecular orbitals built from the metal atom d-orbitals and ligand orbitals.
- In contrast to crystal field theory, which models the structure of the complex in terms of point charges, **ligand field theory assumes, more realistically, that ligands are attached to the central metal atom or ion by covalent bonds.**
- As we shall see, much of the work that we have done in connection with crystal field theory can be transferred into ligand field theory: ***the principal difference is the origin of the ligand field splitting.***
- **Ligand-field theory**, which is an application of **molecular orbital theory** that concentrates on the d orbitals of the central metal atom, provides a more substantial framework for understanding the origins of Δ_0 .

- The ligand field theory overcomes several defects by taking into account **covalent contributions** of metal-ligand interactions.
- To describe the electronic structure of a complex, first we set up molecular orbitals from the available atomic orbitals in the complex, just as we would for a molecule.
- The ***d* orbitals that do not extend into the direction of the coordinated ligands** are now deemed to not take part in bond formation and thus called **non-bonding orbitals**.
- Accordingly, their energy does not change as compared to the set of degenerate *d* orbitals in the free metal ion.
- Notice that the ***t_{2g}*-orbitals** on the metal atom have no partners among the ligands in octahedral environment. There are simply no ligand orbitals to match them. Therefore, these three orbitals are **nonbonding orbitals** in the complex.

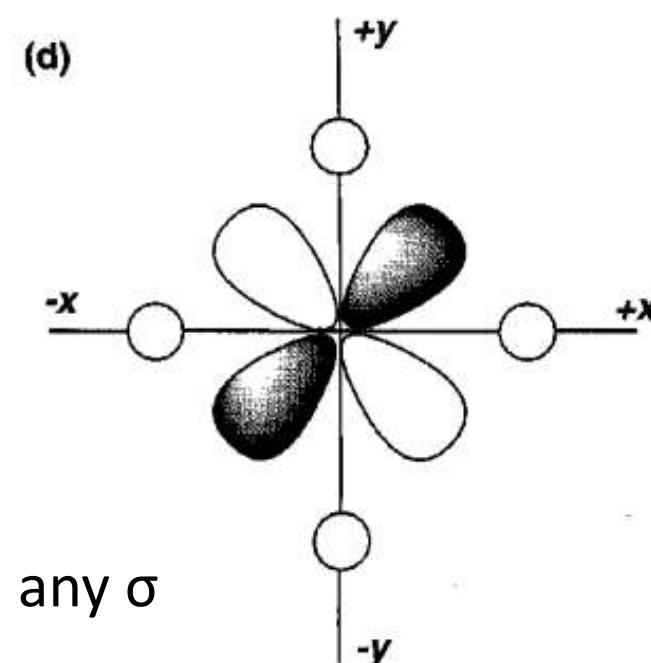


FIG. 13. 6 Fig. (d) shows how the d_{xy} orbital is wrongly aligned to form any σ bond; the other two t_{2g} orbitals are similarly nonbonding.

- The strategy for describing the molecular orbitals of a d-metal complex follows procedures similar to those described earlier for bonding in polyatomic molecules: the valence orbitals on the metal and ligand are used to form *symmetry-adapted* linear combinations (SALCs) and then the relative energies of the molecular orbitals are estimated by using empirical energy and overlap considerations. These relative energies can be verified and positioned more precisely by comparison with experimental data (particularly UV-visible absorption and photoelectron spectroscopy).
- Here we shall first consider octahedral complexes, initially taking into account only the ***metal-ligand σ bonding***.
- We then consider the ***effect of π bonding*** and see that it is *essential for understanding Δ_o* (which is one reason why crystal-field theory cannot explain the spectrochemical series).

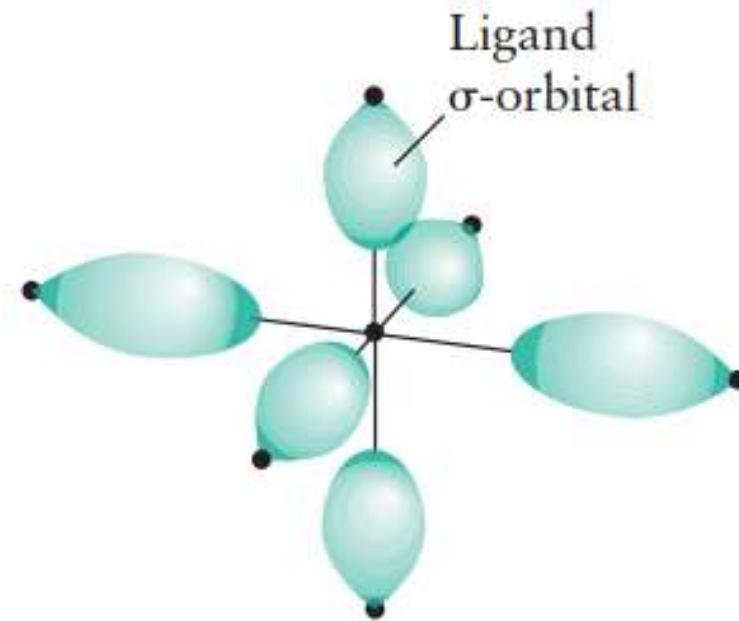
❖ σ Bonding

- We begin by considering an octahedral complex in which each ligand (L) has a single valence orbital directed towards the central metal atom (M); each of these orbitals has local σ symmetry with respect to the M–L axis. Examples of such ligands include the NH_3 molecule and the F^- ion.
- In an octahedral (O_h) environment, the orbitals of the central metal atom divide by symmetry into four sets:

Metal orbital	Symmetry label	Degeneracy
s	a_{1g}	1
p_x, p_y, p_z	t_{1u}	3
$d_{x^2-y^2}, d_{z^2}$	e_g	2
d_{xy}, d_{yz}, d_{zx}	t_{2g}	3

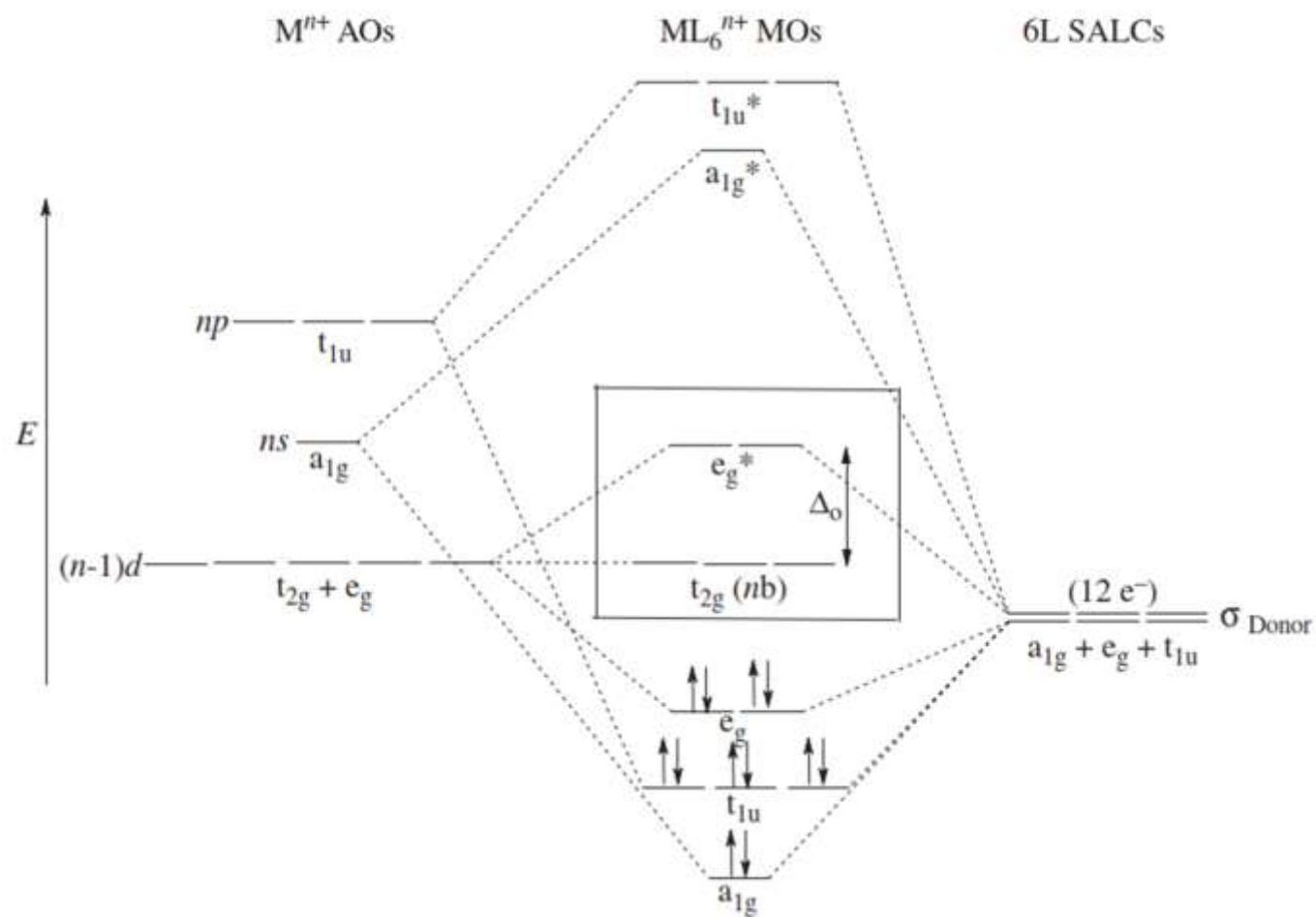
- Consider an octahedral complex of a d-metal in Period 4, such as iron, cobalt, or copper.
- We need to *consider the nine 4s-, 4p-, and 3d-orbitals of the central metal ion, because all these orbitals have similar energies*.
- To simplify the discussion, we *use only one atomic orbital on each of the ligands*. For instance, for a Cl⁻ ligand, we use the Cl 3p-orbital directed toward the metal atom; for an NH₃ ligand, we use the *sp*³ lone-pair orbital of the nitrogen atom.
- ✓ The *six orbitals provided by the six ligands in an octahedral complex* are represented by the tear-shaped lobes in Fig. 16.36. Each of these orbitals has cylindrical symmetry around the metal–ligand axis, so each can form a σ-orbital.

FIGURE 16.36 The tear-shaped objects are representations of the six ligand atomic orbitals that are used to build the molecular orbitals of an octahedral complex in ligand field theory. They might represent s- or p-orbitals on the ligands or hybrids of the two.



- Molecular orbitals are formed by combining SALCs and metal-atom orbitals of the same symmetry. For example, the (unnormalized) form of an a_{1g} molecular orbital is $c_M \psi_{Ms} + c_L \psi_{La1g}$, where ψ_{Ms} is the s orbital on the metal atom M and ψ_{La1g} is the ligand SALC of symmetry a_{1g} .
- ✓ The metal s orbital and ligand a_{1g} SALC overlap to give two molecular orbitals, one bonding and one antibonding.
- ✓ Similarly, the doubly degenerate metal e_g orbitals and the ligand e_g SALCs overlap to give four molecular orbitals (two degenerate bonding, two degenerate antibonding),
- ✓ and the triply degenerate metal t_{1u} orbitals and the three t_{1u} SALCs overlap to give six molecular orbitals (three degenerate bonding, three degenerate antibonding).
- ✓ ***There are therefore six bonding combinations in all and six antibonding combinations.***
- ✓ The *three triply degenerate metal t_{2g} orbitals remain nonbonding and fully localized on the metal atom.*
- ✓ Calculations of the resulting energies (adjusted to agree with a variety of spectroscopic data) result in the molecular orbital energy-level diagram shown in Fig. 16.19.

- There are *nine valence orbitals on the metal atom* (one *s* + three *p* + five *d* orbitals) and *six on the ligands* (one each from six ligands), giving 15 in all.
- We can therefore expect to find 15 molecular orbitals: it turns out, as we have explained above, that *six are bonding, six are antibonding, and three are nonbonding*.
- The energies of all 15 are displayed in Fig..., together with the labels that they are commonly given.



➤ Employing the usual group theoretical approach, the symmetries of the metal ion valence orbitals are listed on the left-hand side of the diagram and their Mulliken symbol designations are determined from the way in which each of the AOs transforms in the O_h point group. Thus, the lower lying d-orbitals transform as $e_g + t_{2g}$, the s-orbital as the spherically symmetric a_{1g} , and the higher lying p-orbitals as the triply degenerate t_{1u} set.

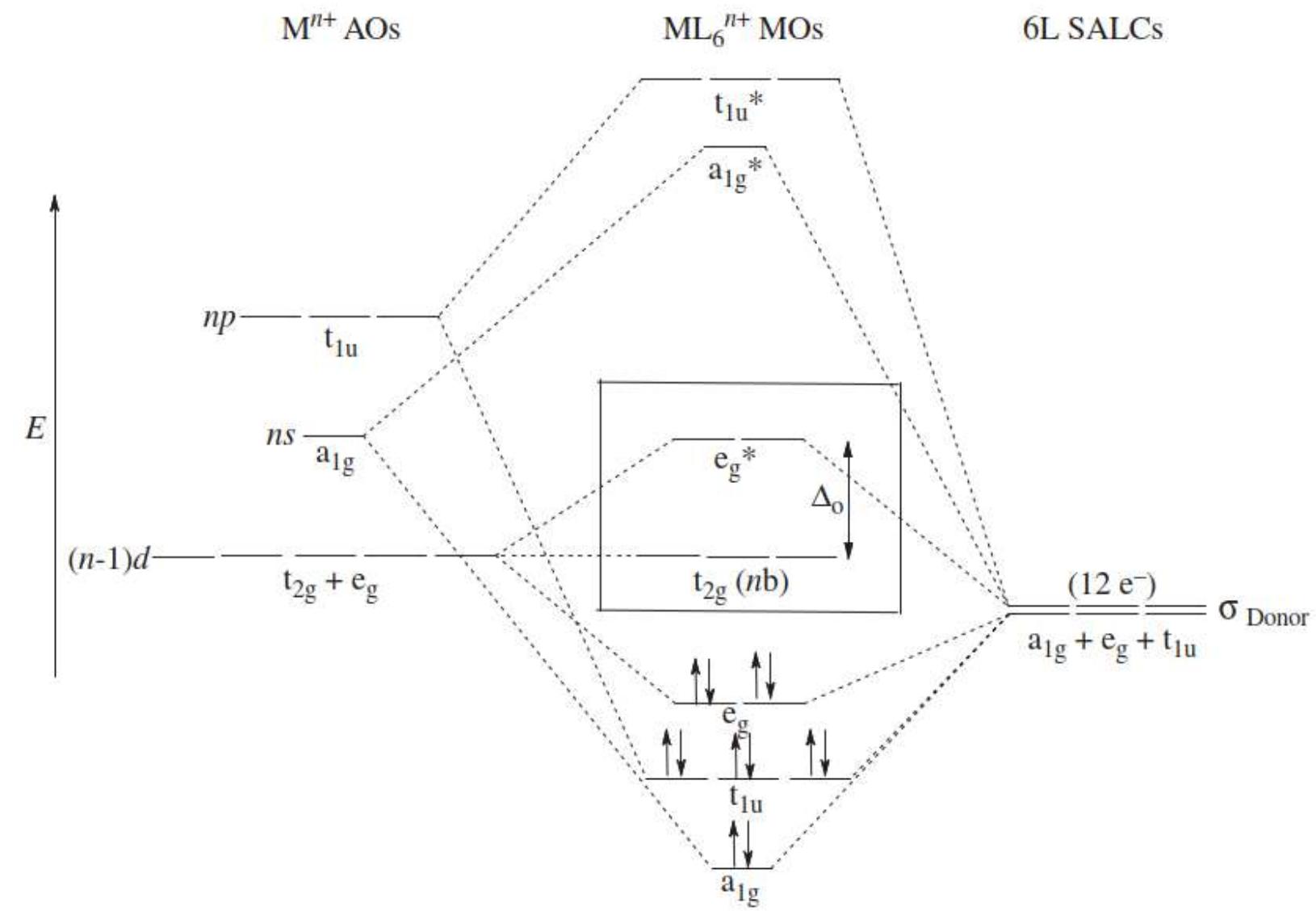


FIGURE 16.19 MO diagram for the formation of $[ML_6]^{n+}$, where the metal–ligand bonding involves only σ -interactions.

- The greatest contribution to the molecular orbital of lowest energy is from atomic orbitals of lowest energy.
- ✓ For NH_3 , F^- , and most other ligands, *the ligand σ orbitals are derived from atomic orbitals with energies that lie well below those of the metal d orbitals.*
- ✓ As a result, *the six bonding molecular orbitals of the complex are mainly ligand-orbital in character* (that is, $c_L^2 > c_M^2$).
- ✓ These six bonding orbitals can accommodate the 12 electrons provided by the six ligand lone pairs.
- ✓ The electrons that we can regard as provided by the ligands are, therefore, largely confined to the ligands in the complex, just as the crystal-field theory presumes.
- ✓ However, because the coefficients c_M 's are nonzero, the bonding molecular orbitals do have some d-orbital character, and the 'ligand electrons' are partly delocalized onto the central metal atom.

- Remember that metals usually have d electrons that are much higher in energy than those on typical donor atoms (like oxygen, sulfur, nitrogen or phosphorus).
 - That means the antibonding combinations will be much closer in energy to the original d orbitals, because both are relatively high in energy.
 - The bonding combination will be much closer in energy to the original ligand orbitals, because these ones are all relatively low in energy.
 - That energetic similarity generally translates into a similarity in shape and location as well.
- ✓ In other words, *the antibonding combination between a d orbital and a ligand orbital is much like the original d orbital.*
- ✓ *The bonding combination is more like the original ligand orbital than the original d orbital.*
- ✓ Because of those similarities, inorganic chemists often refer to those antibonding orbitals as if they were still the original d orbitals.

- The total number of electrons to accommodate, in addition to those supplied by the ligands, now depends on the number of d electrons, n, supplied by the metal atom. These additional electrons enter the orbitals next in line for occupation, which are the nonbonding d orbitals (the t_{2g} orbitals) and the antibonding combination (the upper e_g orbitals) of the d orbitals and ligand orbitals.
- The t_{2g} orbitals are wholly confined (in the present approximation) to the metal atom, and the antibonding e_g orbitals are largely metal-atom in character too, so the n electrons supplied by the central atom remain largely on that atom. The frontier orbitals of the complex are, therefore, the nonbonding entirely metal t_{2g} orbitals and the antibonding, mainly metal e_g orbitals.
- Thus, we have arrived at an arrangement that is qualitatively the same as in crystal-field theory. In the ligand-field approach the octahedral ligand-field splitting parameter, Δ_O , is the separation between the molecular orbitals **largely, but not completely**, confined to the metal atom (Fig. 16.37).

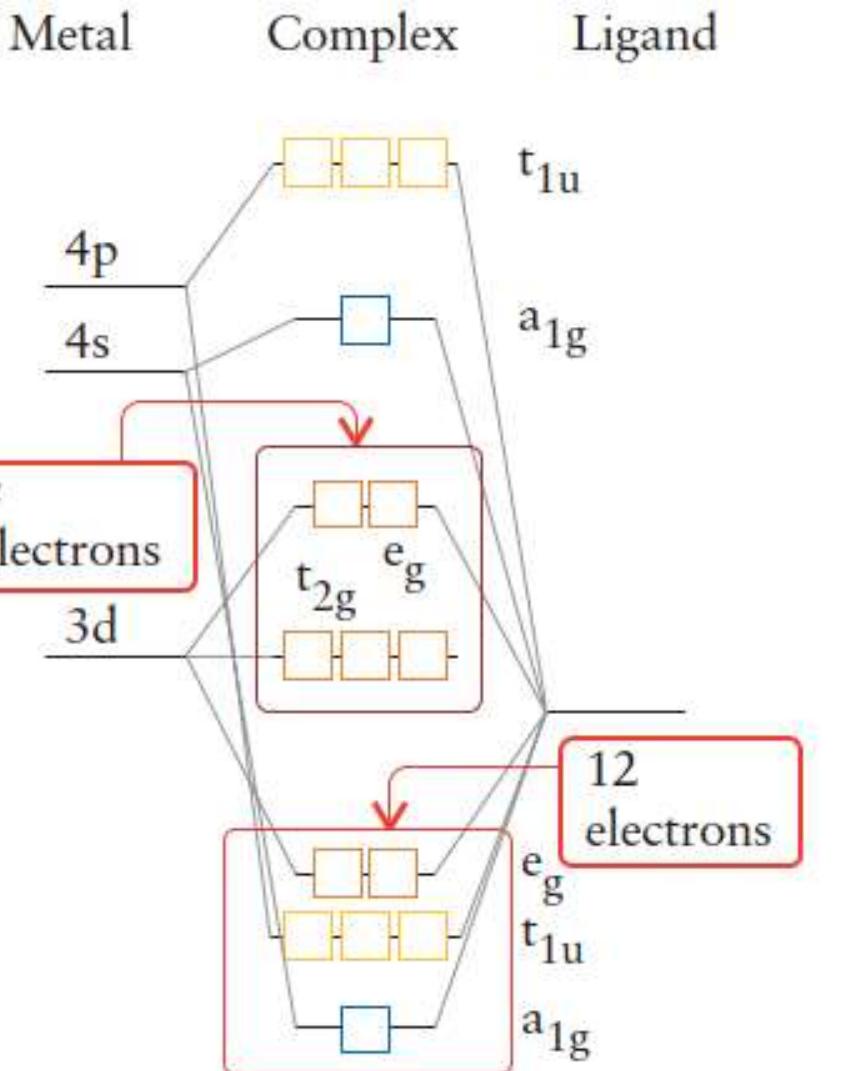


FIGURE 16.37 The molecular orbital energy-level diagram for an octahedral complex. The 12 electrons provided by the six ligands fill the lowest six orbitals, which are all bonding orbitals. The n d-electrons provided by the central metal atom or ion are accommodated in the orbitals inside the upper box. The ligand field splitting is the energy separation of the nonbonding (t_{2g}) and antibonding (e_g) orbitals in the box.

- With the molecular orbital energy-level diagram established, we use the building-up principle to construct the ground-state electron configuration of the complex. For a six-coordinate d^n complex, there are $12 + n$ electrons to accommodate.
- The six bonding molecular orbitals accommodate the 12 electrons supplied by the ligands. The remaining n electrons are accommodated in the nonbonding t_{2g} orbitals and the antibonding e_g orbitals.
- Now the story is essentially the same as for crystal-field theory, the types of complexes that are obtained (high-spin or low-spin, for instance) depending on the relative values of Δ_0 and the pairing energy P .
- The **principal difference from the crystal-field** discussion is that ligand-field theory gives **deeper insight into the origin of the ligand-field splitting**, and we can begin to understand why some ligands are strong, and others are weak.
- For instance, a good σ -donor ligand should result in **strong metal–ligand overlap, hence a more strongly antibonding e_g set** and consequently **a larger value of Δ_0** .
- However, before drawing further conclusions, we must consider what **crystal-field theory ignores completely**: **the role of π bonding**.

- MO theory identifies the t_{2g} orbitals as the nonbonding MOs and the e_g^* orbitals as the antibonding orbitals; **the crystal field splitting Δ_o is the energy difference between them.**
- The energies of the nb orbitals are unaffected by bonding, but the energies of the antibonding orbitals that lie above them are determined by the strength of the metal-ligand bonds.
- Recall that the energy of bonding MOs decreases with increasing bond strength while the energy of the corresponding antibonding MOs increases with increasing bond strength.
- The increase in crystal field splitting observed through the middle of the spectrochemical series correlates well with the strength of the metal-ligand σ bonds, but MO theory cannot account for the order observed throughout the rest of the series without considering π bonding.
- Let's consider the effects of π bonding by first examining the nature of the bonds formed between a metal atom or ion and a single ligand.
- We then extend the treatment to examine the effects of π bonding on the energy level structure and properties of octahedral complexes.

After placing the 12 electrons from the ligand lone pairs in the six bonding orbitals, the nonbonding t_{2g} set of 3d orbitals and the antibonding e_g^* pair are the next five orbitals available to accommodate the d electrons on the metal. *Thus, the descriptions in the electrostatic and molecular orbital theories are very similar.* Both theories produce five orbitals in a lower set of three and an upper set of two, separated by ΔE (Δ_0), to accommodate the d electrons. In the electrostatic theory these sets are, respectively, the atomic d_{xy} , d_{yz} and d_{zx} orbitals and the d_{z^2} and $d_{x^2-y^2}$ atomic orbitals, while, in the molecular orbital theory, the lower set are the same atomic orbitals and the upper set are antibonding molecular orbitals composed of the d_{z^2} and $d_{x^2-y^2}$ atomic orbitals with ligand orbital contributions.

Thus, in their essential description of the varying magnetic properties and d-d transitions, these two theories are identical. The molecular orbital theory has the advantage that it is easily extended to include π -bonding and it gives a prediction of the alteration of energy levels in such a case. It is also more useful for the interpretation of spectra as it provides information, not only about the d levels, but also about the higher energy antibonding orbitals to which excitations occur when higher energy quanta are absorbed. On the other hand, the molecular orbital theory suffers from the disadvantage of all wave mechanics, that it is impossible to calculate bond energies, heats of formation and the like directly.

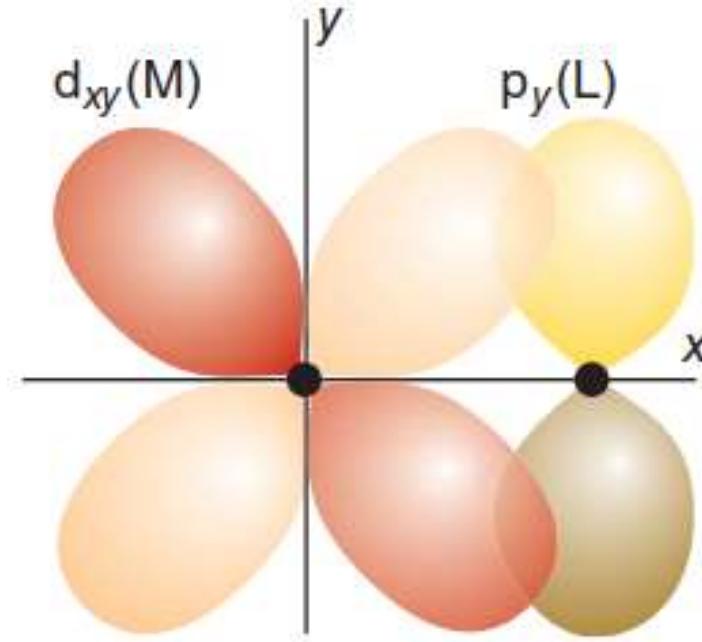
In practice, these two theories may be used interchangeably, as most convenient. Both rely on experimental data to fix the energy levels; for example, ΔE is usually determined spectroscopically.

π Bonding:

- Now we shall answer why CO is a strong-field ligand whereas Cl^- is a weak-field ligand despite its negative charge.
- ❖ Key points: π -Donor ligands decrease Δ_o whereas π -acceptor ligands increase Δ_o ; *the spectrochemical series is largely a consequence of the effects of π bonding when such bonding is feasible.*
- While it is satisfying that the LF (MO) approach yields much the same result as CFT, we have yet to explain why ligands such as CO, CN^- , PR_3 , R^- , NO_2^- , phen, and bpy (particularly those that are neutral) lie so high in the spectrochemical series.
- The answer involves the fact that in addition to acting as σ -donor ligands, this subset of ligands can also undergo what is known as **pi back-bonding**.

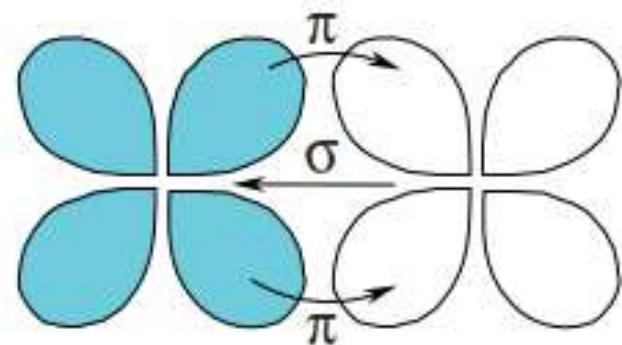
- Following Figures illustrate different types of pi-bonding between metal ions and ligands.
- Pi backbonding can occur from a filled t_{2g} orbital on the metal to
 - ✓ (i) an empty, low-lying d-orbital on the ligands, such as that which occurs for PR_3 , AsR_3 , or SR_2 ;
 - ✓ (ii) an empty π^* MO on a ligand containing multiple bonds, such as that which occurs in CO , CN^- , NO_2^- , bpy, or phen; or
 - ✓ (iii) an empty σ^* MO on the ligands such as that which occurs when H–H or C–H single bonds coordinate to the metal.

Figure 20.19 The π overlap that may occur between a ligand p orbital perpendicular to the M–L axis and a metal d_{xy} orbital.



Metal

Ligand



Filled d

Empty d

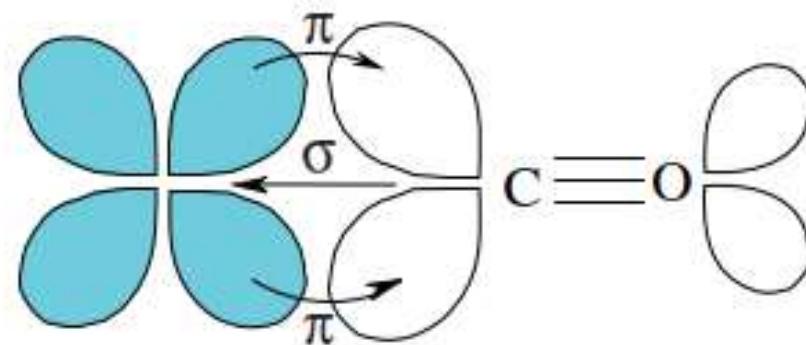
$$d_{\pi} - d_{\pi}$$

$L = PR_3, AsR_3, SR_2$

(a)

Metal

Ligand



Filled d

Empty π^*

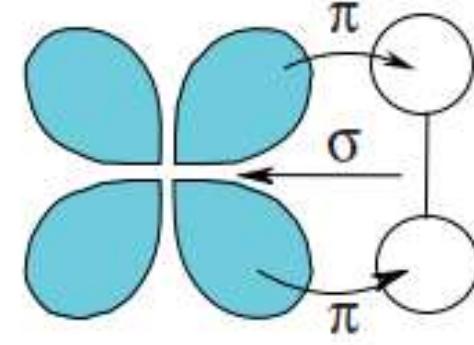
$$d_{\pi} - L_{\pi^*}$$

$L = CO, CN^-, NO^{2-}, bpy, phen$

(b)

Metal

Ligand



Filled d

Empty σ^*

$$d_p - L_{\sigma^*}$$

$L = H_2, \text{alkanes}$

(c)

FIGURE 16.21 (a–c) Three different types of pi backbonding interactions.

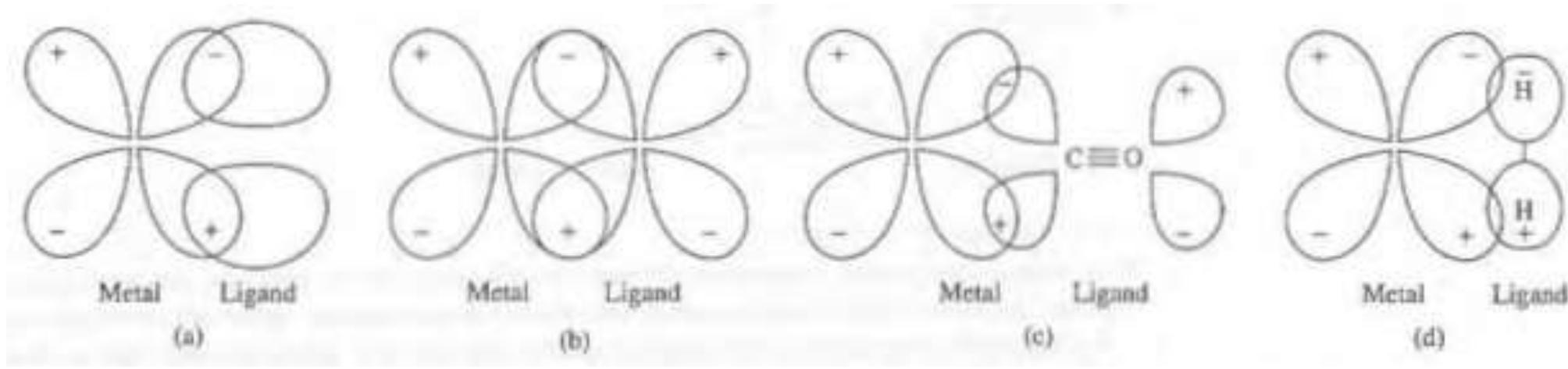


Fig.11.23 Pi overlap of a metal d orbital with various types of *ligand orbitals*: (a) p, (b) d, (c) π^* , and (d) σ^* .

Four potential metal–ligand π interactions: (1) $d_{\pi} - p_{\pi}$, (2) $d_{\pi} - d_{\pi}$, (3) $d_{\pi} - \pi^*$, and (4) $d_{\pi} - \sigma^*$.

- When pi back-bonding does occur, it helps to stabilize the coordination compound by shuttling some of the built-up electron density on the metal from σ -donation back onto the ligands.
- ✓ Because electron density is transferred from the metal to the ligands, pi back-bonding is especially favored by electropositive metals (typically metals from the left-hand side of the periodic table) having low oxidation numbers and strong σ -donor ligands in the other coordination sites.
- We need to develop the model by considering the effects of other ligand orbitals. When we constructed the molecular orbitals above, we considered only ligand orbitals that pointed directly at the central metal atom.
- Ligands also have orbitals perpendicular to the metal–ligand (M–L) axis with local π symmetry, which we expect to form bonding and antibonding π orbitals with the metal orbitals.
- For an octahedral complex, the combinations that can be formed from the ligand π orbitals include SALCs of t_{2g} symmetry. These ligand combinations have net overlap with the metal t_{2g} orbitals, which are therefore no longer purely nonbonding on the metal atom.

- Depending on the relative energies of the ligand and metal orbitals, the energies of the now molecular t_{2g} orbitals lie above or below the energies they had as nonbonding atomic orbitals, so Δ_0 is decreased or increased, respectively.
- To explore the ***role of π bonding*** in more detail, we need two of the general principles described earlier in MO theory. First, we shall make use of the idea that, **when atomic orbitals overlap effectively, they mix strongly: the resulting bonding molecular orbitals are significantly lower in energy and the *antibonding molecular orbitals are significantly higher in energy than the atomic orbitals*.** Second, we note that atomic orbitals with similar energies interact strongly, whereas those of very different energies mix only slightly, even if their overlap is large.
- There are no disputes over which ligand orbitals have the correct symmetry to participate in π bonding, but the extent to which this actually occurs for some ligands is vigorously debated. Even when ligand and metal orbitals have the proper symmetry for π bond formation, ***an energy or size mismatch may lead to insignificant interaction.***

- In the metal carbonyl complexes, the direct bearing of the π -back donation is observed on the M–C bond distance that becomes shorter as compared to that of a normal M–C single bond distance.
- ✓ For example, the $\text{CpMo}(\text{CO})_3\text{CH}_3$ complex, exhibits two kind of M–C bond distances that comprise of a longer Mo– CH_3 distance (2.38 Å) and a much shorter Mo–CO distance (1.99 Å) arising out of a metal to ligand π -back donation.
- It becomes thus apparent that the metal–CO interaction can be easily characterized using X-ray crystallography.
- The infrared spectroscopy can also be equally successfully employed in studying the metal–CO interaction. Since the *metal to CO π -back bonding involves a π -donation from the metal d_π orbital to a π^* orbital of a C–O bond, a **significant shift of the $\nu(\text{CO})$ stretching frequency towards the lower energy** is observed in metal carbonyl complexes with respect to that of free CO (2143 cm^{-1}).*
- The energies of the ν_{CO} band for the metal carbonyls correlate with the strength of the carbon-oxygen bond and inversely correlated with the strength of the π -back-bonding between the metal and the carbon.

Backbonding and IR Absorption

- CO ligands are carbon monoxide ligands that participate readily in transition metal complexes via coordinate bonds with a transition metal center.
- CO ligands are neutral 2 electron donors and first form a sigma bond with a metal center.
- As discussed above, the d orbitals of the transition metal are symmetric about the π^* orbitals of the CO compound and back-bonding occurs between the metal and the CO. This process is illustrated in Figure 1.20.1. Pi back-donation is supported by IR (infrared spectroscopy) data of various metal-carbonyl complexes. Using group theory, one can consider the consequences of back-bonding and the effects this would have on the IR absorption of a carbonyl-containing compound.

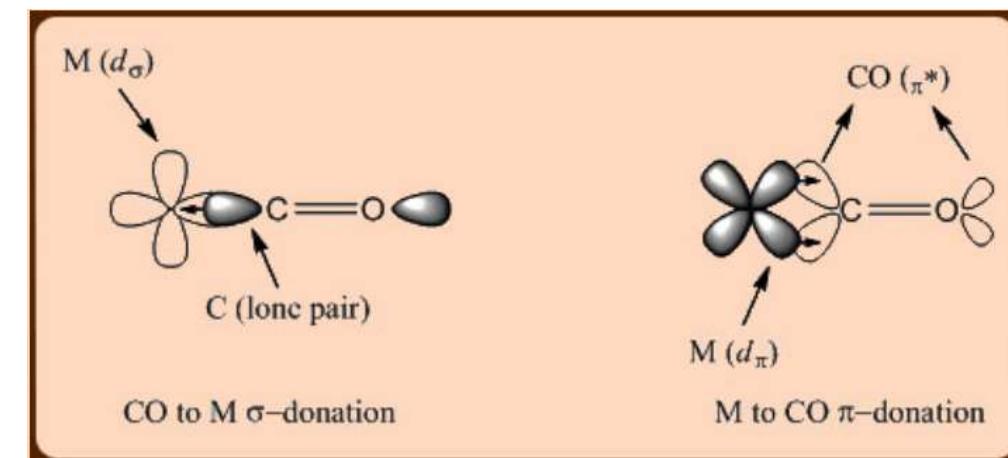
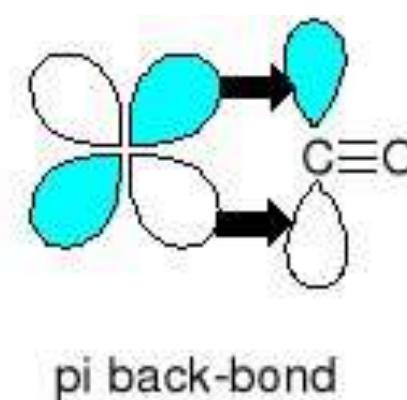
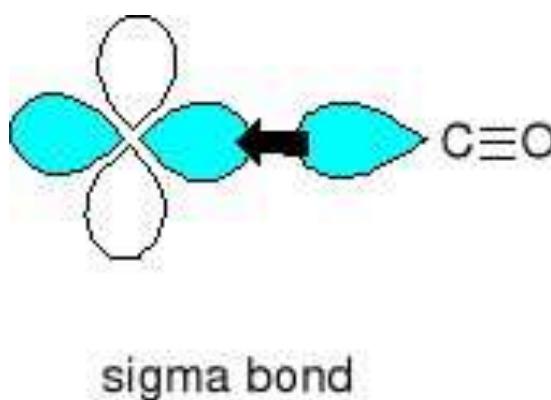


Figure 1.20.1: Sigma Donation and Pi Backbonding

- ***Pi back-bonding donates electrons from the transition metal center to the pi* antibonding orbital of CO, the LUMO of this ligand (Lowest Unoccupied Molecular Orbital).***
- ✓ This, in turn, ***lowers the bond order between carbon and oxygen, weakening*** their interaction.
- ✓ This would cause one to suspect that metal carbonyl complexes would absorb light of a lower frequency upon excitation by infrared radiation.
- ✓ This is consistent with experimental data, with few exceptions, for several metal carbonyl complexes when compared to the IR absorption of free carbonyls. This is depicted in Table 1.20.1.

Table 1.20.1. IR Absorption Frequencies for Metal Carbonyls

Compound	ν_{CO} (cm ⁻¹)
CO	2143
V(CO) ₆ ¹⁻	1859
Cr(CO) ₆	2000
Mn(CO) ₆ ⁺	2100
Fe(CO) ₆ ²⁺	2204
Fe(CO) ₅	2022, 2000
Ru(CO) ₅	2038, 2022

- Some convincing arguments for covalency and the most convincing evidence in support of pi backbonding comes from the IR spectra of the metal carbonyls, $M(CO)_6$.
- For the isoelectronic series of compounds listed in Table 16.6, the **$\nu(CO)$ stretching frequency decreases as the electron density on the metal accumulates.**
- The CO molecule has a strong triple bond which in the IR gives rise to a strong absorption at $\sim 2140\text{ cm}^{-1}$.
- For the series $[Mn(CO)_6]^+$, $[Cr(CO)_6]$ and $[V(CO)_6]^-$, which are isoelectronic, the IR bands for the CO have shifted to 2090, 2000 and 1860 cm^{-1} respectively.
- Despite the fact that the metals have the same number of electrons (isoelectronic) the frequency of force constant of the CO bond is seen to vary $Mn^+ > Cr > V^-$.
- This can not be explained on an ionic basis but is *consistent with the π bonding scheme since the greater the positive charge on the metal, the less readily the metal can delocalize electrons back into the π^* orbitals* of the CO group.

TABLE 16.6 IR frequencies for the $\nu(\text{CO})$ stretch in a series of isoelectronic metal carbonyls.

Compound	M^{n+}	$\nu(\text{CO}), \text{cm}^{-1}$
$\text{Mn}(\text{CO})_6^+$	Mn^+	2090
$\text{Cr}(\text{CO})_6$	Cr^0	2000
$\text{V}(\text{CO})_6^-$	V^-	1860
$\text{Ti}(\text{CO})_6^{2-}$	Ti^{2-}	1748

- Note that the IR values we are dealing with relate to the CO bond and not the M-C so when the CO frequency gets less then it is losing triple bond character and becoming more like a double bond. This is expected if electrons are pushed back from the metal into what were empty π^* antibonding orbitals.

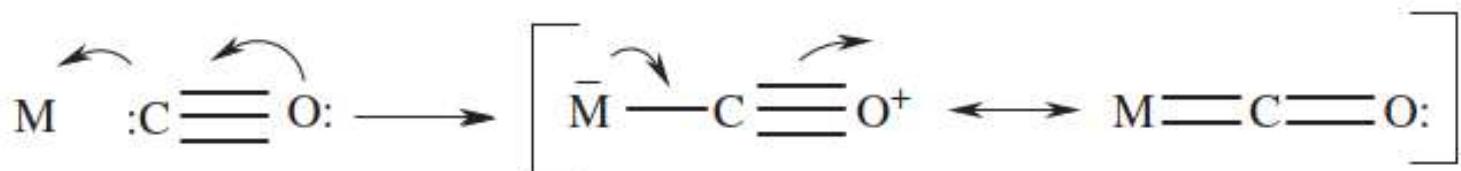
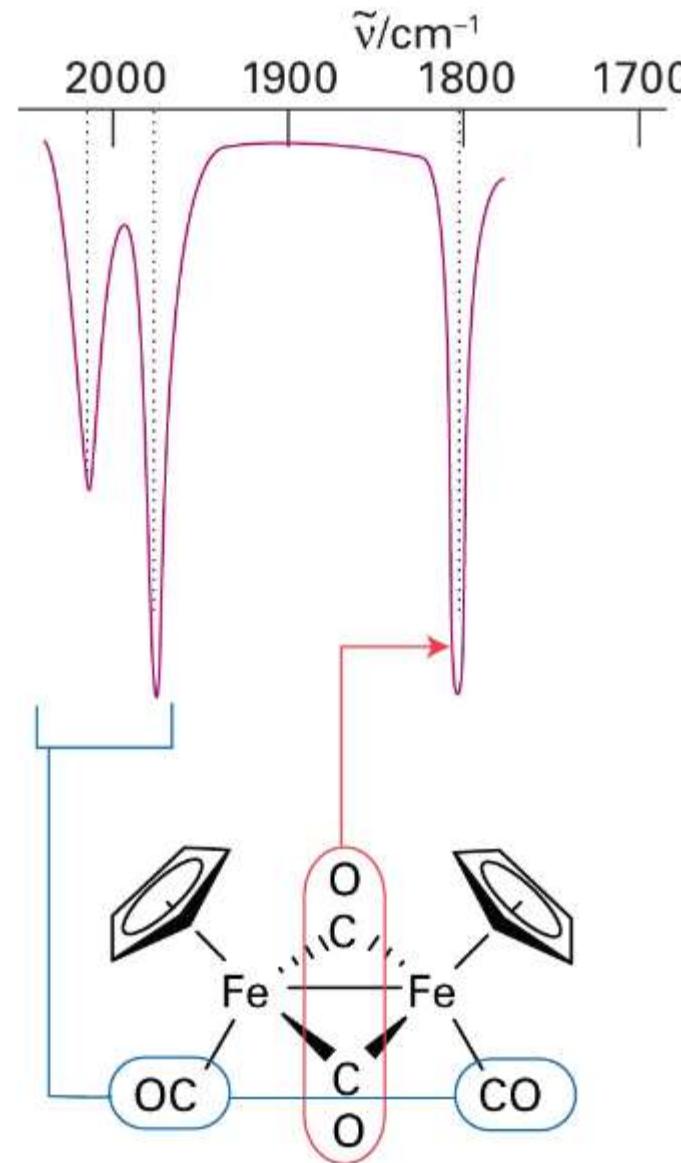


FIGURE 16.22 Two canonical forms for metal-carbonyl bonding, showing the pi character in the resonance hybrid.

- SOME FACTS Typical stretching frequencies:
 - Uncoordinated or "free" CO: 2143 cm⁻¹
 - Terminal M-CO: 2125 to 1850 cm⁻¹
 - Doubly bridging (μ -2): 1850 to 1750 cm⁻¹
 - Triply bridging (μ -3): 1675 to 1600 cm⁻¹
 - Semi-bridging: somewhere between terminal and μ -2.
- Trends observed in the IR spectra of carbonyl complexes that are consistent with the concept of π -back-bonding:
 1. With each charge added to the metal center, the CO stretching frequency decreases by approximately 100 cm⁻¹.
 2. The better the sigma-donating capability (or worse the pi-acceptor ability) of the other ligands on the metal, the lower the CO stretching frequency.
 3. For simple carbonyl complexes, counting the number of IR and Raman CO stretching frequencies will often permit one to make a structural assignment.
The number of CO stretches expected for possible geometries/isomers can be predicted using group theory and the calculated results compared to the experimental data.

Infrared spectra report on types of CO groups in the organometallic.



❖ The effect of π -bonding on ligand field splitting

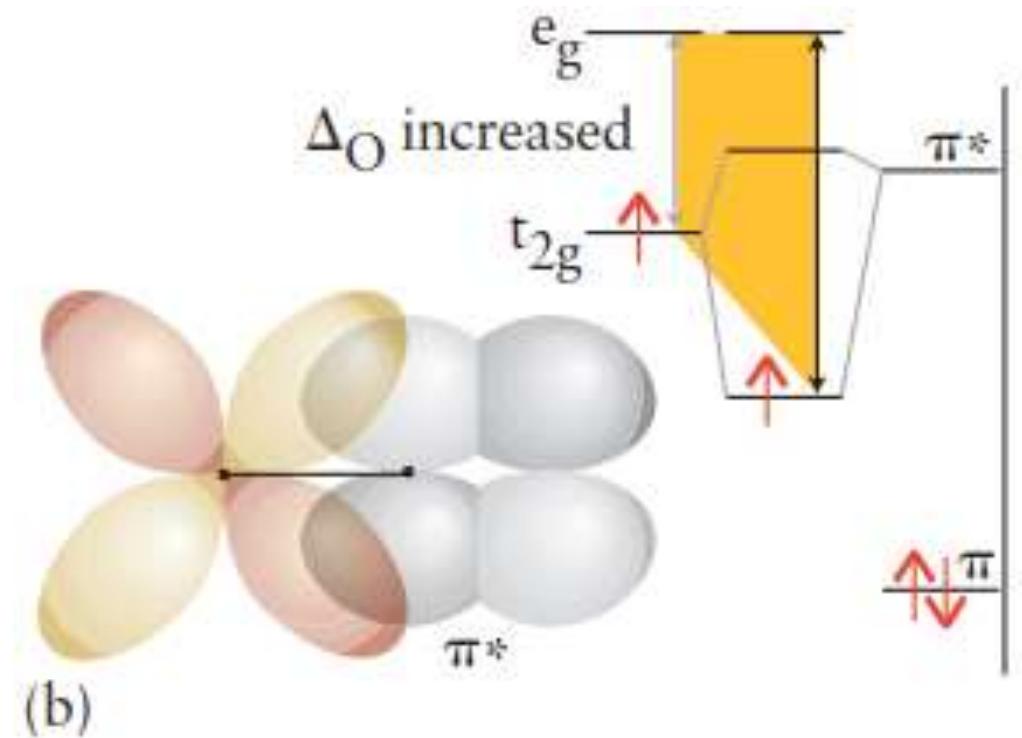
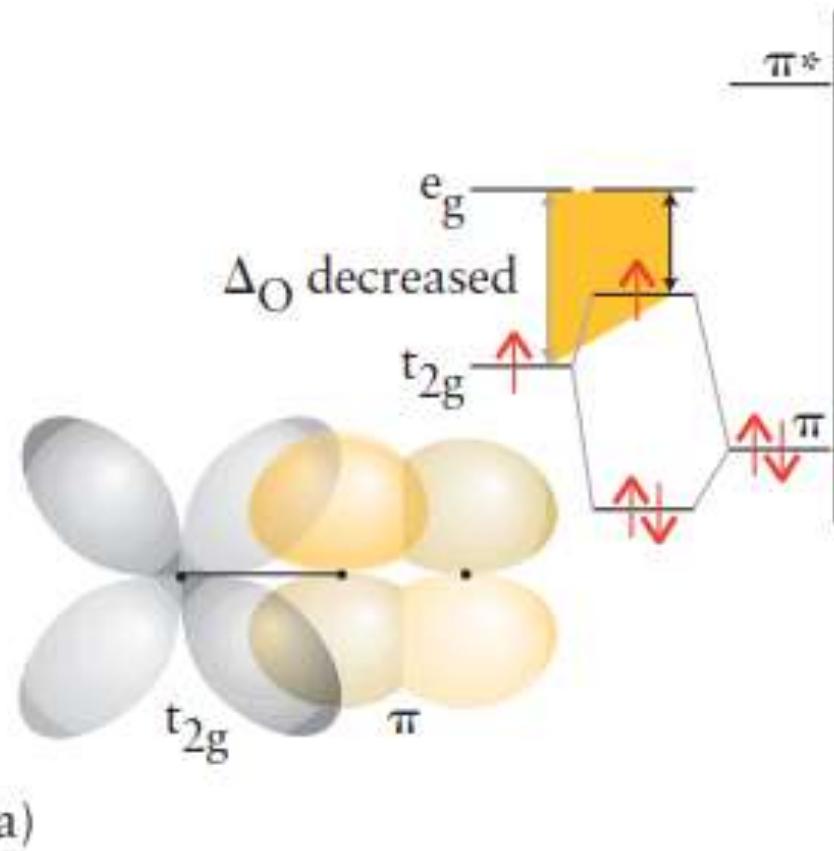


FIGURE 16.38 The effect of π -bonding on ligand field splitting. (a) In this case, the occupied π -orbital of the ligand is close in energy to the t_{2g} orbitals, and they overlap to form bonding and antibonding combinations. *The ligand-field splitting is reduced.*

(b) In this case, the unoccupied antibonding π^* -orbital of the ligand is close in energy to the t_{2g} orbitals, and they overlap to form bonding and antibonding combinations. In this case, the *ligand-field splitting is increased.*

❖ The effect of π -bonding on ligand field splitting

- As Figs. 8.31 (a and b) show that a p-orbital on the ligand perpendicular to the axis of the metal–ligand bond can overlap with one of the t_{2g} -orbitals to produce two new molecular orbitals, one bonding and one antibonding. The resulting bonding orbital lies below the energy of the original t_{2g} -orbitals; the antibonding orbital lies above them.

Fig. 8.31 (a): In this case *when the occupied π -orbital of the ligand is full*, the π -orbital is close in energy to the t_{2g} orbitals and they overlap to form bonding and antibonding combinations. In this case, **the ligand-field splitting is reduced**.

Fig. 8.31 (b): In this case, the unoccupied antibonding π^* -orbital of the ligand is close in energy to the t_{2g} orbitals and they overlap to form bonding and antibonding combinations. In this case, **the ligand-field splitting is increased**.

Left: LGOs of t_{2g} symmetry;
 Right: MOs for the σ system of the complex;
 Center: MOs after π interaction.

- Note that Δ_0 is diminished by the π interaction.
- When the occupied π -orbital of the **ligand is full**, the π -orbital is close in energy to the ligand t_{2g} orbitals and they overlap to form bonding and antibonding combinations, **the ligand-field splitting (Δ_0) is reduced**.

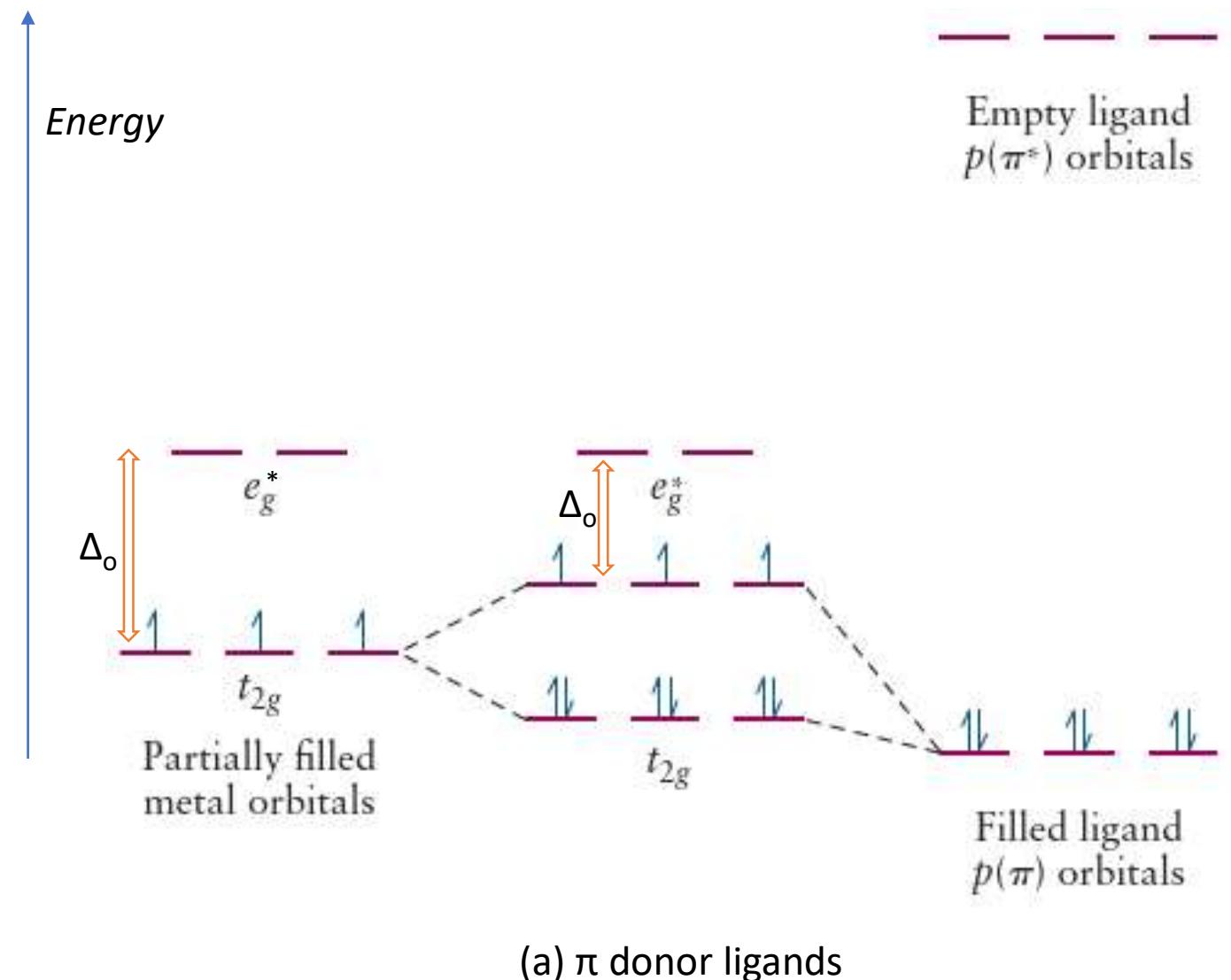
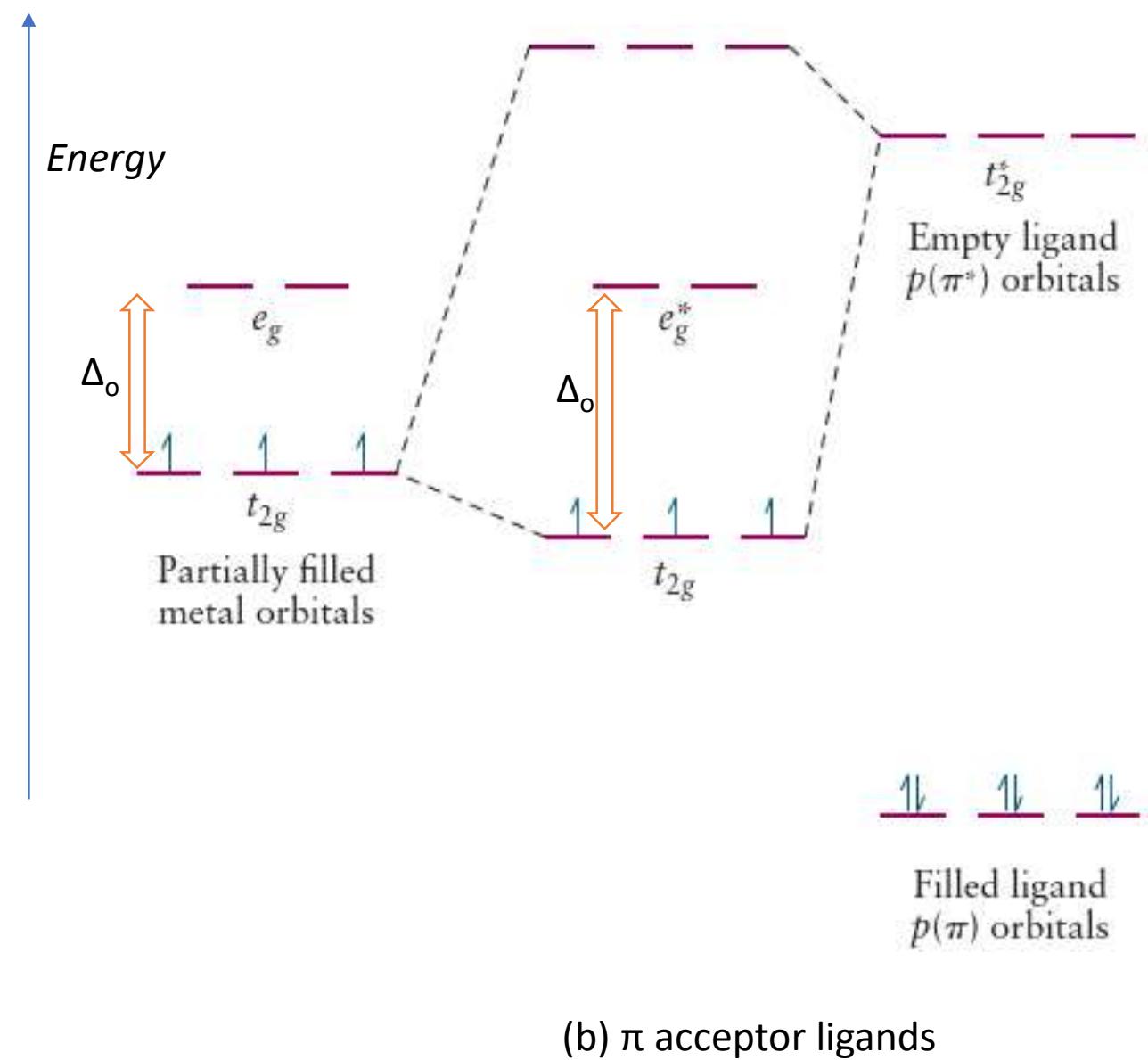


FIGURE 8.31 (a) Ligand-to-metal π donation showing the formation of bonding and antibonding MOs and a reduction in Δ_0 compared with that from s bonding alone.

MO diagram for the π system of an octahedral complex with acceptor ligands such as CO, PR₃, or SR₂.

- Note that the π interaction in this case increases Δ_0 .
- When the unoccupied antibonding π^* -orbital of the ligand is close in energy to the ligand t_{2g} orbitals and they overlap to form bonding and antibonding combinations, **the ligand-field splitting is increased.**



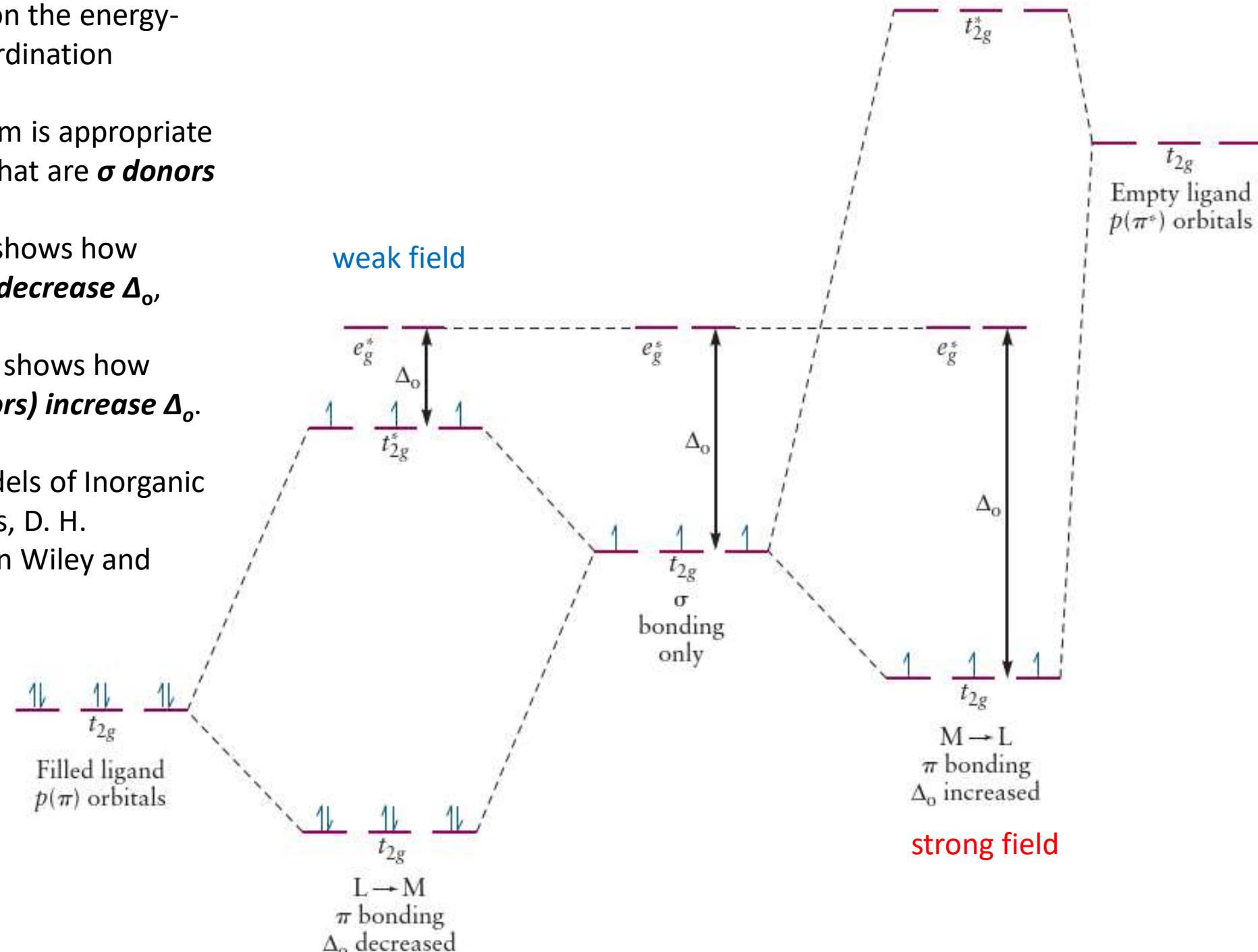
(b) π acceptor ligands

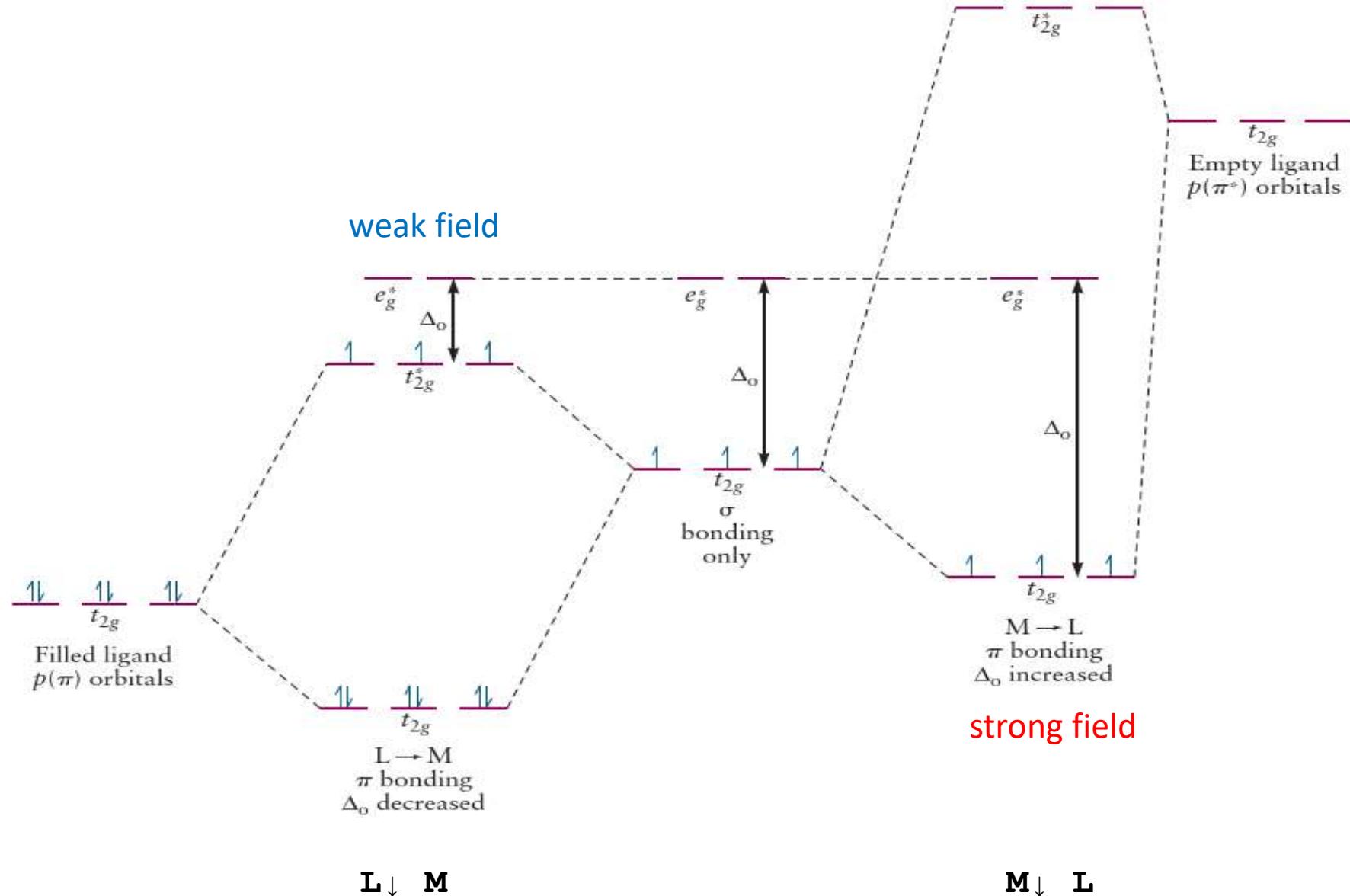
FIGURE 8.31(b) Metal-to-ligand π donation showing the formation of bonding and antibonding MOs and an increase in Δ_0 compared with that from s bonding alone.

FIGURE 8.32 Effect of π bonding on the energy-level structure for octahedral coordination complexes.

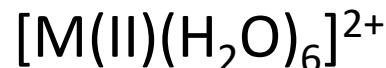
- ✓ The **center** energy-level diagram is appropriate for intermediate field ligands that are **σ donors only**.
- ✓ The **left** energy-level diagram shows how **weak field ligands (π donors) decrease Δ_o** , and
- ✓ the **right** energy-level diagram shows how **strong field ligands (π acceptors) increase Δ_o** .

(Adapted from Concepts and Models of Inorganic Chemistry, 2nd edition, B. Douglas, D. H. McDaniel, and J. J. Alexander, John Wiley and Sons, New York, 1983, p. 293.)





For example:



- Now we count the number of electrons to accommodate. If the ligand is Cl^- , the $\text{Cl}3\text{p}$ -orbital that we have used to build the metal–ligand π -orbital is full. It provides two electrons, which occupy a new molecular orbital, the bonding metal–ligand combination. The n d-electrons provided by the metal must therefore occupy the antibonding metal–ligand orbital. Because this molecular orbital is higher in energy than the original t_{2g} -orbitals, the ligand field splitting is decreased by π -bonding. Therefore, we see how Cl^- can be a weak-field ligand despite its negative charge.
- Now suppose the ligand is CO. The orbital that overlaps with the metal t_{2g} -orbitals in this case is either the full bonding π -orbital or the empty antibonding π^* -orbital of the CO molecule. It turns out that the latter orbital is closer in energy to the metal orbitals, and so it plays the dominant role in bond formation to the metal. There are no electrons from the ligand to accommodate because its π^* -orbital is empty. The n d-electrons therefore enter the bonding metal–ligand orbital. Because this new molecular orbital is lower in energy than the original t_{2g} -orbitals, the ligand field splitting is increased by π -bonding and CO is a strong-field ligand despite being electrically neutral.

NOTE: The increase in Δ_0 caused by π bonding is substantial enough in many cases that the absorption maximum for the t_{2g} -to- e_g^* electronic transition is blue-shifted out of the visible region into the ultraviolet portion of the electromagnetic spectrum, with the result that the complexes are **colorless**. This is the case for the metal carbonyls, for example.

A **π -donor ligand** is a ligand that, before any bonding is considered, has **filled orbitals of π symmetry** around the M–L axis. Such ligands include Cl^- , Br^- , OH^- , O^{2-} , and even H_2O . In Lewis acid–base terminology, a π -donor ligand is a **π base**. *The energies of the full π orbitals on the ligands will not normally be higher than their σ -donor orbitals (HOMO) and must therefore also be lower in energy than the metal d orbitals.* Because the full π orbitals of π -donor ligands lie lower in energy than the partially filled d orbitals of the metal, when they form molecular orbitals with the metal t_{2g} orbitals, the bonding combination lies lower than the ligand orbitals and the antibonding combination lies above the energy of the d orbitals of the free metal atom (Fig. 20.20). The electrons supplied by the ligand π orbitals occupy and fill the bonding combinations, leaving the electrons originally in the d orbitals of the central metal atom to occupy the antibonding t_{2g} orbitals. The net effect is that the previously **nonbonding** metal t_{2g} orbitals **become antibonding** and hence are raised closer in energy to the antibonding e_g orbitals. It follows that π -donor ligands decrease Δ_0 .

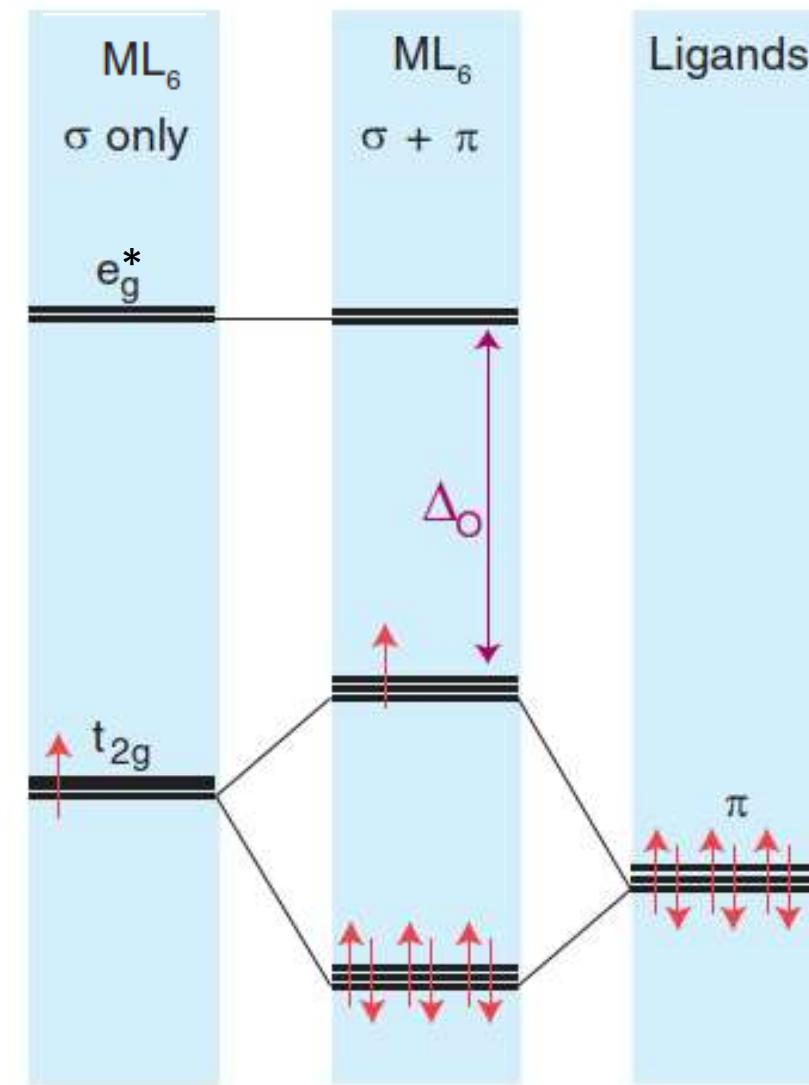


Figure 20.20 The effect of π bonding on the ligand-field splitting parameter. Ligands that act as π donors decrease Δ_0 . Only the π orbitals of the ligands are shown.

A **π -acceptor ligand** is a ligand that **has empty π orbitals** that are available for occupation. In Lewis acid–base terminology, a π -acceptor ligand is a π acid. *Typically, the π -acceptor orbitals are vacant antibonding orbitals on the ligand (usually the LUMO), as in CO and N₂, which are higher in energy than the metal d orbitals.* The two π^* orbitals of CO, for instance, have their largest amplitude on the C atom and have the correct symmetry for overlap with the metal t_{2g} orbitals, so **CO can act as a π -acceptor ligand**. **Phosphines (PR₃)** are also able to **accept π -electron density** and also act as π acceptors.

Because the π -acceptor orbitals *on most ligands* are higher in energy than the metal d orbitals, they form molecular orbitals in which the *bonding t_{2g} combinations are largely of metal d-orbital character* (Fig. 20.21). These bonding combinations lie lower in energy than the d orbitals themselves. The net result is that π -acceptor ligands increase Δ_0 .

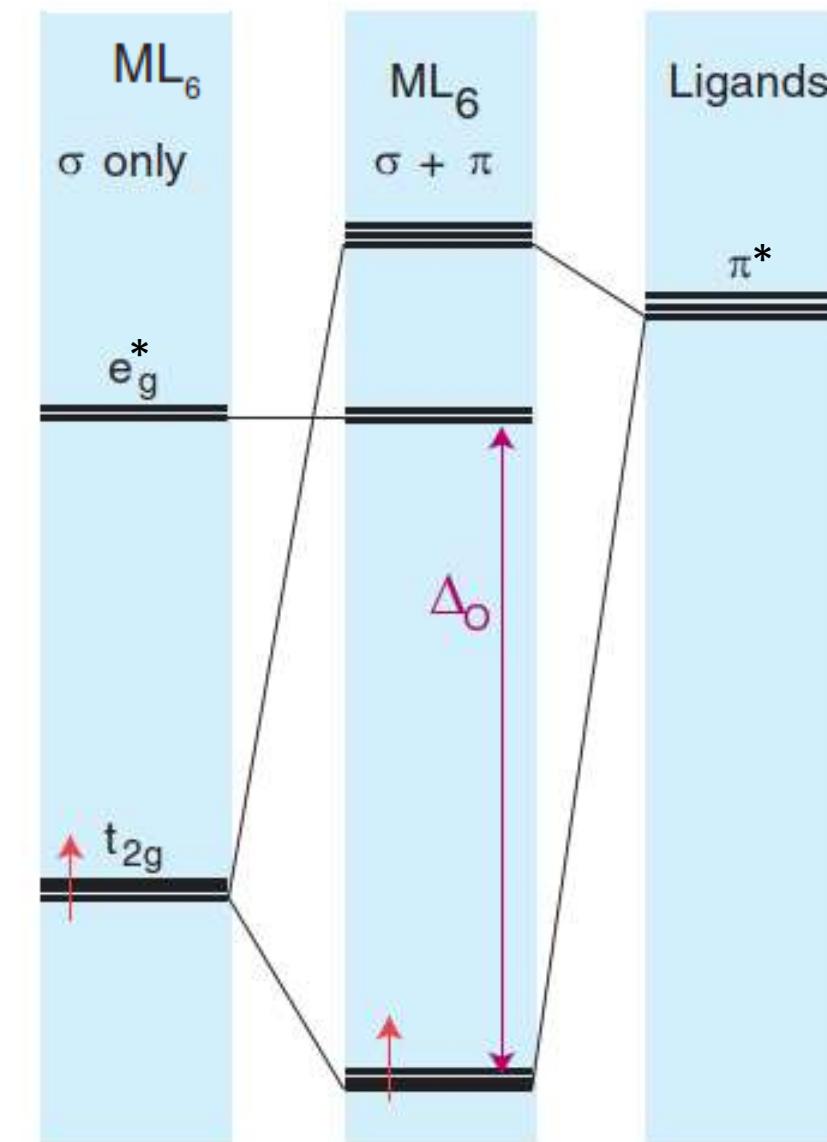


Figure 20.21 The effect of π bonding on the ligand-field splitting parameter. Ligands that act as π acceptors increase Δ_0 . Only the π orbitals of the ligands are shown.

We can now put the role of π bonding in perspective. The order of ligands in the spectrochemical series is partly that of the strengths with which they can participate in M–L σ -bonding. For example, both CH_3^- and H^- are *high in the spectrochemical series* (similar to NCS^-) because they are *very strong σ donors*. However, *when π bonding is significant*, it has a strong influence on Δ_o : **π -donor ligands decrease Δ_o and π -acceptor ligands increase Δ_o** . This effect is responsible for CO (a strong π acceptor) being high on the spectrochemical series and for OH^- (a strong π donor) being low in the series. The overall order of the spectrochemical series may be interpreted in broad terms as dominated by π effects (with a few important exceptions), and in general the series can be interpreted as follows:

—increasing $\Delta_o \rightarrow$
 π donor, weak π donor, no π effects, π acceptor

Representative ligands that match these classes are

π donor	π acceptor	π acceptor	π acceptor
I^- , Br^- , Cl^- , F^-	H_2O	NH_3	PR_3 , CO

Notable examples of where the effect of σ bonding dominates include amines (NR_3), CH_3^- , and H^- , none of which has orbitals of π symmetry of an appropriate energy and thus are neither π -donor nor π -acceptor ligands. It is important to *note* that ***the classification of a ligand as strong-field or weak-field does not give any guide as to the strength of the M–L bond.***

❖ Strong field ligands

- Strong field ligands are ones that produce large splittings between the d orbitals and form low spin complexes. Examples of strong field ligands include CO, CN⁻, and NO₂.
- From a ligand field theory perspective all three of these ligands have strong π bonds (either double or triple bonds) and ***have empty π^* molecular orbitals available for back-bonding.*** Strong field ligands are both sigma donors (all ligands are sigma donors) and π acceptors. π back-bonding between a metal and a ligand stabilizes the metal based t_{2g} molecular orbital and increases Δ_o .

❖ Weak field ligands

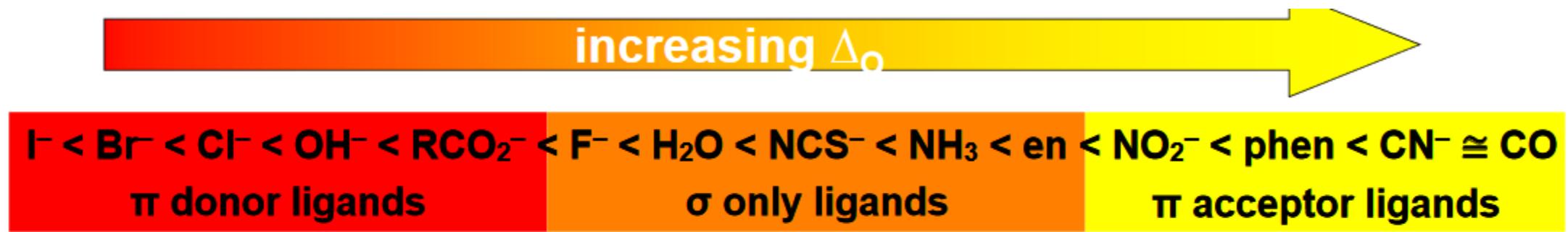
- Weak field ligands are ones that produce small splittings between the d orbitals and form high spin complexes. Examples of weak field ligands include the halogens, OH⁻ and H₂O.
- From a ligand field perspective these ions or molecules all have filled orbitals which can π bond with the metal d orbitals. In the case of the halogens these are filled p orbitals and ***in the case of OH⁻ and H₂O these are lone pairs which are perpendicular to the metal-ligand bond.*** Weak field ligands are both **sigma donors** and **π donors**. The π donation from the ligand to the metal destabilizes the metal based t_{2g} molecular orbital and decreases Δ_o .

❖ Intermediate field ligands

- Intermediate field ligands produce intermediate splittings between the d orbitals and could form high or low spin complexes.
- Examples of intermediate field ligands include NH_3 or ethylenediamine (en).
- From a ligand field perspective ***these ligands only have a single lone pair available for sigma bonding.***
- ***Intermediate ligands are those which are only sigma donors and are not π donors or π acceptors.***
- In this case the t_{2g} symmetry d orbitals are nonbonding and the ***Δ_o is determined by the strength of the metal-ligand sigma interaction*** (and amount of destabilization of the e_g^* molecular orbital).

❖ Spectrochemical Series

➤ The trend in Δ_o that arises from π -donor, σ -only, and π -acceptor ligands is the basis for the Spectrochemical Series. For $[ML_6]^{n+}$ complexes:



- weak-field ligands
- high-spin complexes for 3d metals*

- strong-field ligands
- low-spin complexes for 3d metals*

The value of Δ_o also depends systematically on the metal:

1. Δ_o increases with increasing oxidation number.

2. Δ_o increases down a group.

→ both trends are due to stronger metal-ligand bonding.

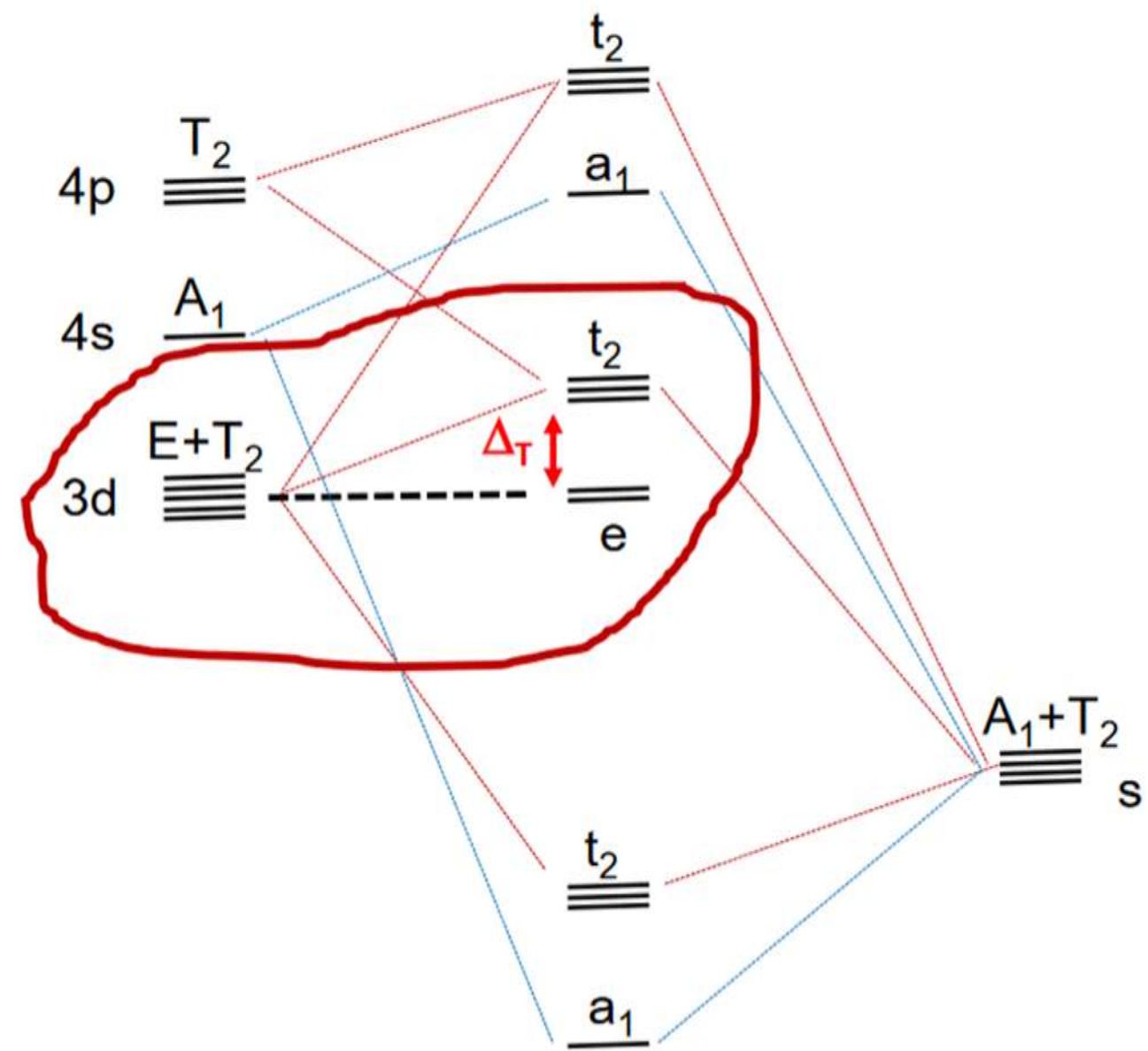
* Due to effect #2, octahedral 3d metal complexes can be low spin or high spin, but 4d and 5d metal complexes are always low spin.

Tetrahedral ML_4

Metal

ML_4

4 Ligands



The effect of π bonding on geometries other than octahedral is qualitatively similar, though we should note that in the *tetrahedral geometry it is the e orbitals that form the π interactions*. In the case of square-planar complexes the order of some of the notionally metal d orbitals changes compared with the pure crystal-field picture. Figure 20.22 shows the arrangement of metal d orbitals with π interactions considered; if we compare this picture with that in Fig. 20.10, where only electrostatic interactions with a crystal field were considered, we see that in both cases it is the $d_{x^2 - y^2}$ orbital that is highest in energy, and therefore unoccupied in complex with a d⁸-metal ion.

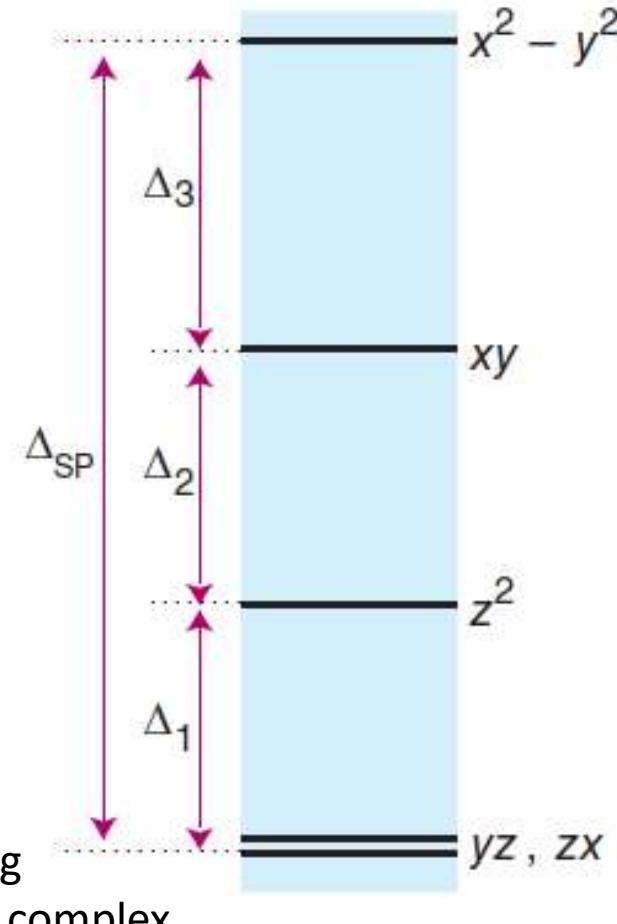


Figure 20.10 The orbital splitting parameters for a square-planar complex.

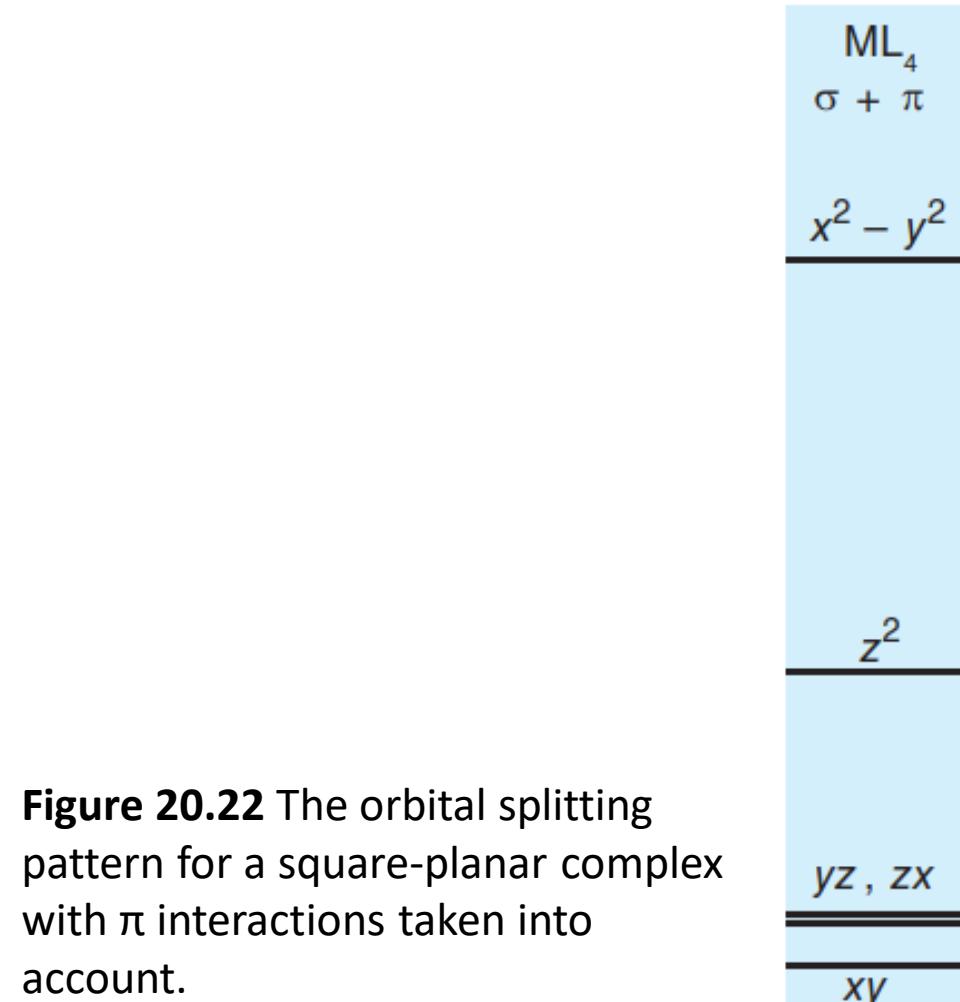


Figure 20.22 The orbital splitting pattern for a square-planar complex with π interactions taken into account.

Cisplatin: A Cancer-Fighting Drug

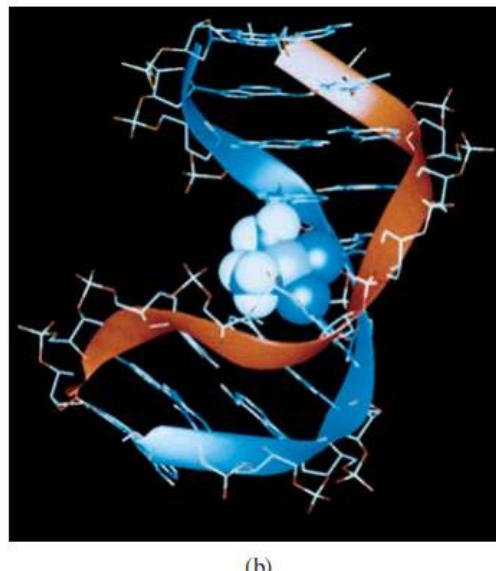
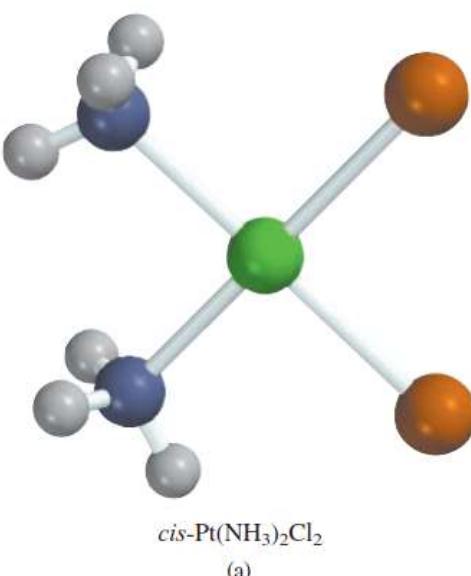
Chemotherapy is a treatment used for some types of cancer. The treatment employs anticancer drugs to destroy cancer cells. An important cancer-fighting drug is *cisplatin*, which is commonly used to treat testicular, bladder, lung, esophagus, stomach, and ovarian cancers. In the mid-1960s, scientists discovered that *cis*-diamminedichloroplatinum(II), $\text{cis}-[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, also called *cisplatin*, is an effective drug for certain types of cancers.

The **mechanism for the action** of cisplatin is the chelation of DNA (deoxyribonucleic acid). *Cisplatin binds* to DNA by forming cross-links in which *the two chloride ions on cisplatin are replaced by nitrogen donor atoms* on the DNA molecule (Figure 20.21). *This action leads to a mistake (mutation) in the DNA's replication and the eventual destruction of the cancerous cell.* Interestingly, the geometric isomer, *trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, has no anticancer effect because it lacks the ability to bind to DNA.

Worldwide annual sales of platinum-based anticancer drugs are currently in excess of \$2 billion.

Figure 20.21

- (a) $\text{cis}-[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.
- (b) Cisplatin disrupts DNA replication and transcription by binding to the double helix. The structure of this major DNA adduct, depicted here, was elucidated by Professor Stephen Lippard's group at MIT.



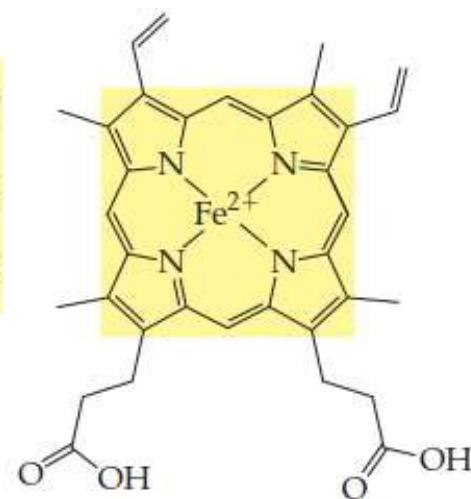
Transition Metal Complexes in Biological Systems

In addition to four building-block elements (C, O, H, and N) and seven elements known as macronutrients (Na, Mg, P, S, Cl, K, and Ca), organisms contain a large number of trace elements, most of which are transition metals. With the exception of Sc, Ti, and Ni (in most species), the Period 4 transition elements are essential to many organisms (Table 22.10), and plants require Mo (from Period 5) as well. The principles of bonding and d-orbital splitting are the same in complex biomolecules containing transition metals as in simple inorganic systems. We focus here on an iron-containing complex.

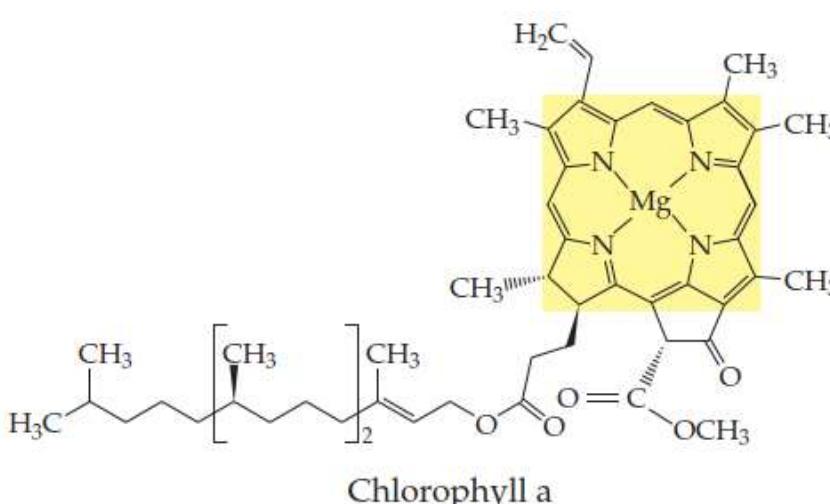
The d-block metals catalyze redox reactions, form components of membrane, muscle, skin, and bone, catalyze acid–base reactions, control the flow of energy and oxygen, and carry out nitrogen fixation.



Porphine



Heme b



Chlorophyll a

Table 22.10 Essential Transition Metals in Humans

Element	Function
Vanadium	Fat metabolism
Chromium	Glucose utilization
Manganese	Cell respiration
Iron	Oxygen transport; ATP formation
Cobalt	Component of vitamin B ₁₂ ; development of red blood cells
Copper	Hemoglobin synthesis; ATP formation
Zinc	Elimination of CO ₂ ; protein digestion

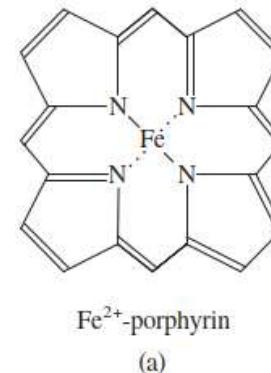
Coordination compounds play many roles in animals and plants. They are essential in the storage and transport of oxygen, as electron transfer agents, as catalysts, and in photosynthesis. Here we will briefly discuss the coordination compounds containing the porphyrin group and cisplatin as an anticancer drug.

Hemoglobin and Related Compounds

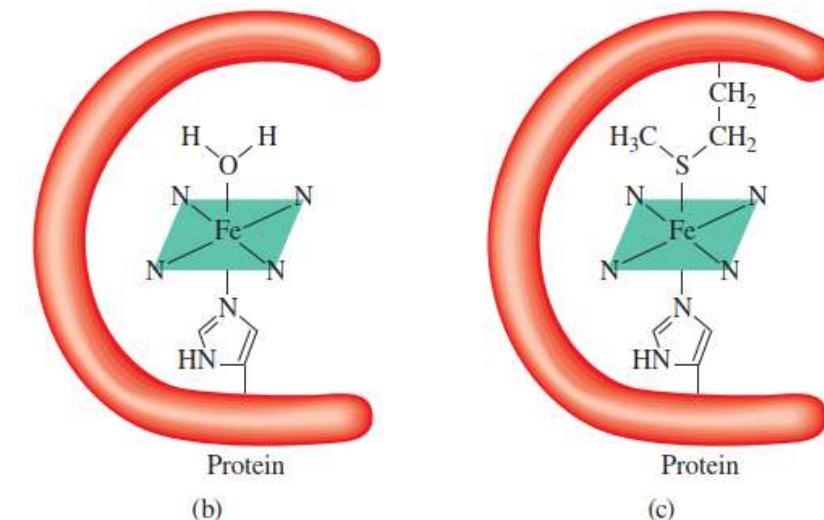
Hemoglobin functions as an oxygen carrier for metabolic processes. The molecule contains four folded long chains called subunits. Hemoglobin carries oxygen in the blood from the lungs to the tissues, where it delivers the oxygen molecules to myoglobin. Myoglobin, which is made up of only one subunit, stores oxygen for metabolic processes in muscle.

The heme group in each subunit is a complex ion formed between a Fe^{2+} ion and a porphyrin group [Figure 20.20(a)]. ***The Fe^{2+} ion is coordinated to the four nitrogen atoms in the porphyrin group and also to a nitrogen donor atom in a ligand that is part of the protein molecule. The sixth ligand is a water molecule,*** which binds to the ion on the other side of the planar ring to complete the octahedral geometry [Figure 20.20(b)]. In this state, the molecule is called ***deoxyhemoglobin and imparts a purplish-bluish tinge to venous blood.*** The ***water ligand can be replaced readily by molecular oxygen to form the red oxyhemoglobin found in arterial blood.***

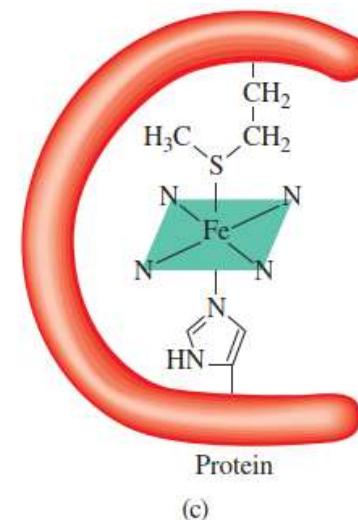
Figure 20.20 (a) Structure of Fe^{2+} -porphyrin. (b) The heme group in hemoglobin. The Fe^{2+} ion is coordinated with the nitrogen atoms of the heme group. The ligand below the porphyrin is the histidine group, which is part of the protein. The sixth ligand is a water molecule, which can be replaced by oxygen. (c) The heme group in cytochromes. The ligands above and below the porphyrin are the methionine group and histidine group of the protein molecule.



Fe^{2+} -porphyrin
(a)



Protein
(b)



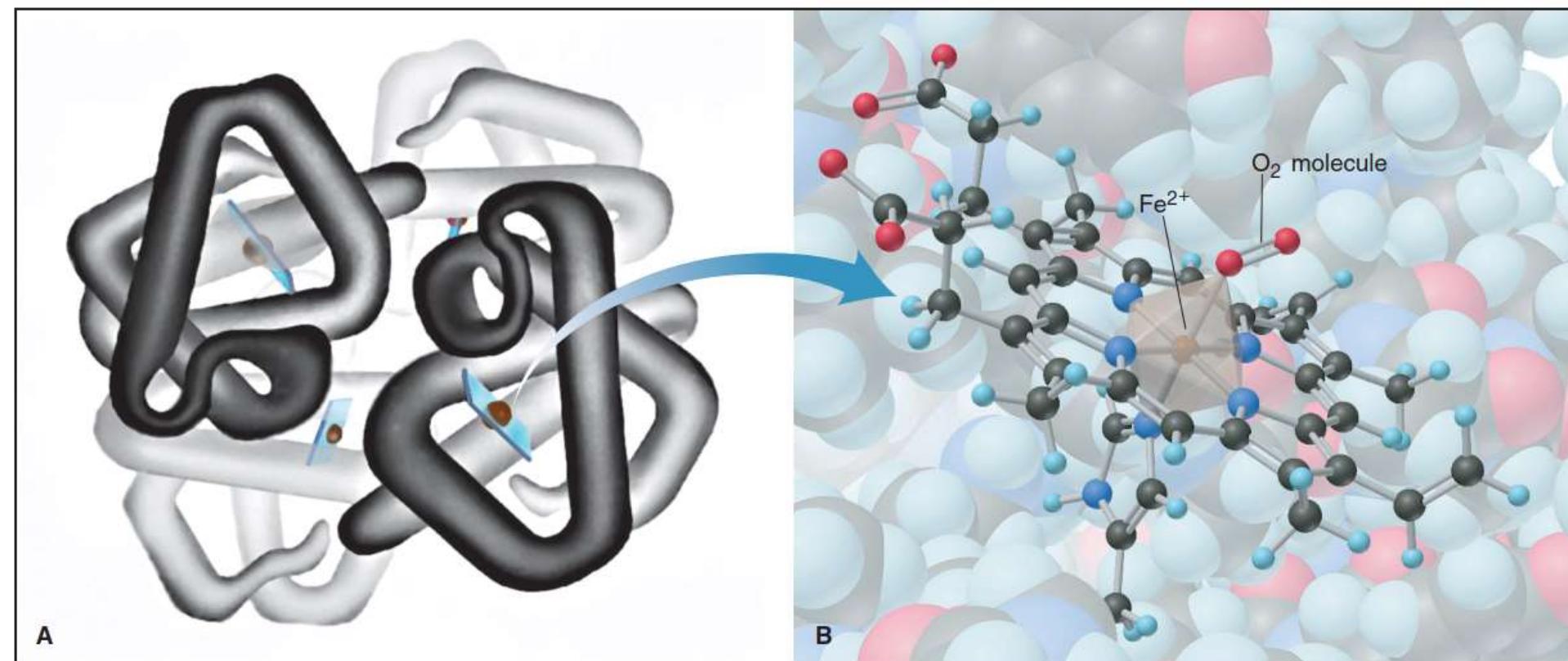
Protein
(c)

Iron plays a crucial role in oxygen transport in all vertebrates. The O₂-transporting protein hemoglobin (Figure 22.25A) consists of four folded chains, each cradling the Fe-containing complex heme. Heme consists of iron(II) bonded to four N lone pairs of a tetradentate ring ligand known as a **porphin** to give a square planar *complex (porphyrins)*. (Porphins are common biological ligands that are also found in chlorophyll, with Mg²⁺ at the center, and in vitamin B₁₂, with Co³⁺ at the center.)

In *hemoglobin* (Figure 22.25B), the *complex is octahedral*, with the fifth ligand of iron(II) being an N atom from a nearby amino acid (histidine), and the sixth an O atom from either an O₂ (shown) or an H₂O molecule.

Figure 22.25 Hemoglobin and the octahedral complex in heme.

A: Hemoglobin consists of four protein chains, each with a bound heme.
(Illustration by Irving Geis. Rights owned by Howard Hughes Medical Institute. Not to be used without permission.) B: In oxyhemoglobin, the octahedral complex in heme has an O₂ molecule as the sixth ligand for iron(II).



- In the arteries and lungs, the Fe^{2+} ion in heme binds to O_2 ; in the veins and tissues, O_2 is replaced by H_2O . Because H_2O is a weak-field ligand, the $d^6 \text{Fe}^{2+}$ ion is part of a high-spin complex, and the *relatively small d-orbital splitting makes venous blood absorb light at the red (low-energy) end of the spectrum and look purplish blue.*
- ..On the other hand, O_2 is a strong-field ligand, so it increases the splitting energy and gives a low-spin complex. Thus, *arterial blood absorbs at the blue* (high-energy) end of the spectrum, which *accounts for its bright red color.*
- In hemoglobin, the heme is linked to a protein (globin) through an additional Fe–N bond. In addition, the Fe(II) can bond to an O_2 molecule to give the six-coordinate, octahedral complex present in oxyhemoglobin. The three-dimensional shape of the protein part of the molecule makes possible the reversible binding of O_2 .

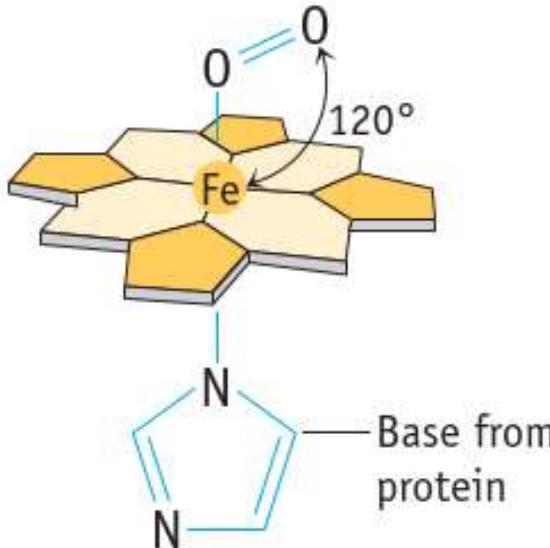


Figure. Oxygen binding. Oxygen binds to the iron of the heme group in *oxyhemoglobin* (and in myoglobin). Interestingly, the $\text{Fe}-\text{O}-\text{O}$ angle is bent.

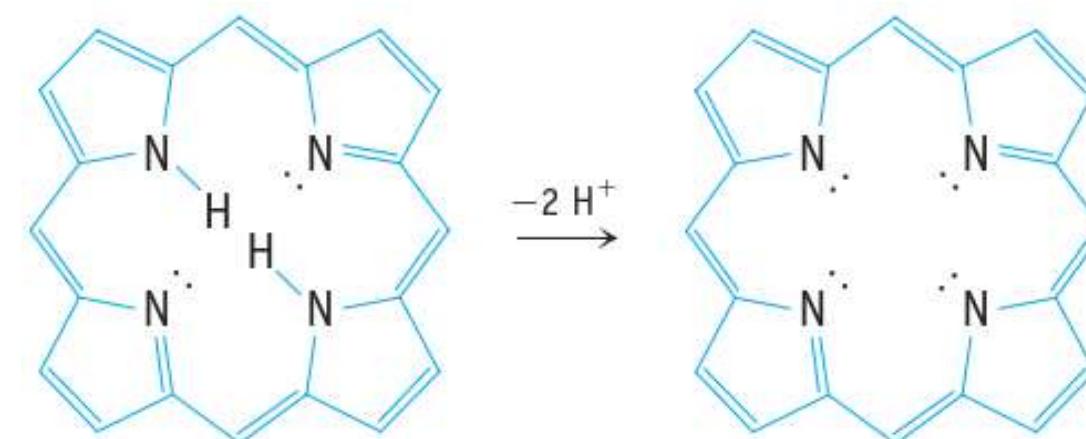
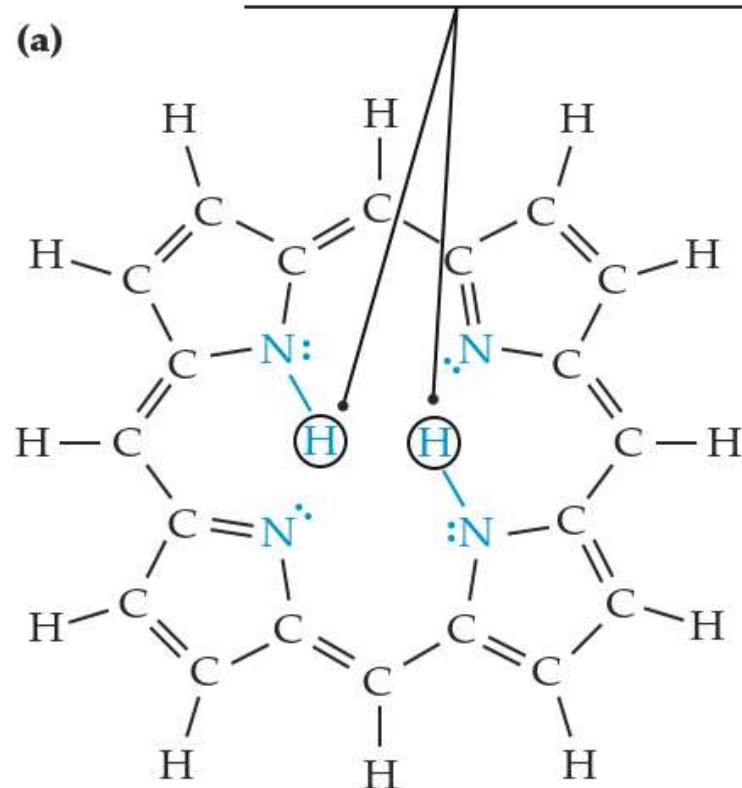


Figure. Porphyrin ring of the heme group. The tetradentate ligand surrounding the iron(II) ion in hemoglobin is a dianion of a molecule called a porphyrin. Because of the double bonds in this structure, all of the carbon and nitrogen atoms in the dianion of the porphyrin lie in a plane. The nitrogen lone pairs are directed toward the center of the ion, and *the molecular dimensions are such that a metal ion may fit nicely into the cavity.*

Loss of the two NH protons gives a planar, tetradentate 2⁻ ligand that can bond to a metal cation.

(a)



The Fe(II) ion has a six-coordinate, octahedral environment, and the O₂ acts as a monodentate ligand.

(b)

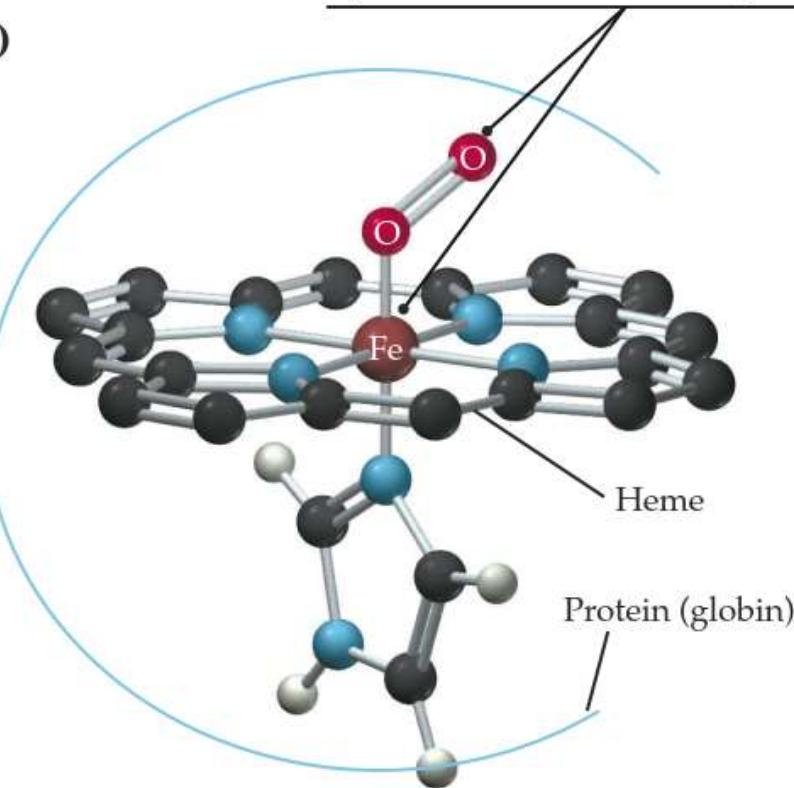


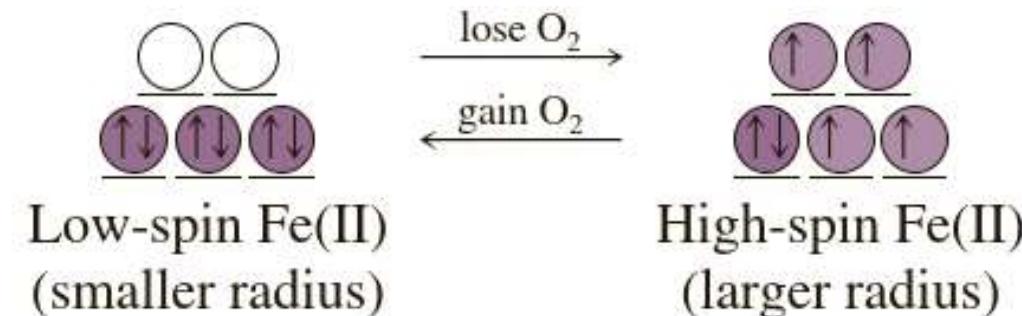
FIGURE 20.15 Chelating ligands in biomolecules. (a) The structure of the **porphin** molecule. The **porphyrins** are **derivatives of porphin** in which some of **the peripheral H atoms are replaced by various substituent groups**. (b) Schematic of the planar heme group, the attached protein chain, and the bound O₂ molecule in oxyhemoglobin. The **porphin is a tetradentate ligand for the central metal**, and the **metal–porphin complex is called a porphyrin**. Specific porphyrins differ in their central metals and in the substituent groups on the porphin rings.

Although hemoglobin is a tetramer of myoglobin, it does not function simply as four independent units of myoglobin. For it to function efficiently as a transporter of O₂ from the lungs and then be able to release that O₂ easily to myoglobin, hemoglobin *must be less strongly attached to O₂* in the vicinity of a muscle cell than is myoglobin.

In hemoglobin, the release of O₂ from one heme group triggers the release of O₂ from another heme group of the same molecule. In other words, there is a ***cooperative release of O₂*** from hemoglobin that makes it possible for it to give up its O₂ to myoglobin.

The ***mechanism postulated for this cooperative release of O₂ depends on a change of iron(II) from a low-spin to a high-spin form***, with a ***corresponding change in the radius of the iron atom***. In oxyhemoglobin, iron(II) exists in the low-spin form. When O₂ leaves, the iron atom goes to a high-spin form with two electrons in the higher-energy d orbital. ***These higher-energy orbitals are somewhat larger than the lower-energy d orbitals.***

- When an O₂ molecule leaves a heme group, the radius of the iron atom increases, and the atom pops out of the heme plane by about 70 pm. In hemoglobin, this change triggers the cooperative release of another O₂ molecule.
- As the iron atom moves, the attached globin group moves with it. This motion of one globin group causes an adjacent globin group in the tetramer to alter its shape, which in turn makes possible the easy release of an O₂ molecule from its heme unit.



- There is another interesting event that happens when oxygen binds to the iron in hemoglobin. After binding O₂, the iron actually transfers a single electron to the oxygen, becoming a Fe³⁺ cation. Although deoxyhaemoglobin, the Fe²⁺ or Fe(II) species, is purple, many Fe³⁺ or Fe(III) compounds are red. Thus, oxyhaemoglobin is red.
- It is also interesting to note that we are used to seeing iron-containing materials turn a sort of red-brown color when they have been exposed to oxygen for a long time, especially in the presence of water and salts. Our cars, trains and bridges eventually rust as the iron in their steel turns to reddish iron oxide. William Tolman, a researcher in bioinorganic chemistry at the University of Minnesota, likes to raise the following question: we rely on iron complexes to carry oxygen through our salt-water bloodstream, so ***why don't we get rusty?***
- The ***answer*** is that, in a sense, ***we do***.
- It has been estimated that after several passes through our bloodstream, a hemoglobin molecule meets its end when the oxygen fails to detach and the iron complex decomposes to an iron oxide. That's one reason why you need to eat a diet that contains iron, to replenish your iron stores in order to make new hemoglobin on a regular basis.

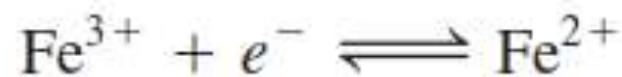
- ***Carbon monoxide is toxic*** because it binds to Fe^{2+} ion in heme about 200 times more strongly than O_2 , which prevents the heme group from functioning:



Like O_2 , CO is a strong-field ligand, which results in a bright red color of the blood. Because the binding is an equilibrium process, breathing extremely high concentrations of O_2 displaces CO from the heme and reverses CO poisoning:



The iron-heme complex is present in another class of proteins called the *cytochromes*. Here too, the iron forms an octahedral complex, but both the fifth and sixth ligands are part of the protein structure [Figure 20.20(c)]. Because the ligands are firmly bound to the metal ion, they cannot be displaced by oxygen or other ligands. Instead, the ***cytochromes act as electron carriers***, which are essential to metabolic processes. In cytochromes, iron undergoes rapid reversible redox processes:



which are coupled to the oxidation of organic molecules such as the carbohydrates.

- The chlorophyll molecule, which is necessary for plant photosynthesis, also contains the porphyrin ring, but in this case the metal ion is Mg^{2+} rather than Fe^{2+} .
- Green is the complementary color of magenta—a purplish red—so we should expect **chlorophyll** to absorb light in the red region of the spectrum (about 670–680 nm). This suggests that ***green plants should grow more readily in red light*** than in light of other colors, and *some experimental evidence indicates that this is the case*. For example, the maximum rate of formation of $O_2(g)$ during photosynthesis occurs with red light.

Experimental Technique: UV-VISIBLE ABSORPTION SPECTROSCOPY

Ultraviolet (UV)-visible absorption spectroscopy is a spectroscopic method that measures the light absorption by the molecular species in a solution in the UV (200–380 nm) to visible (380–750 nm) wavelength range. The ultraviolet region below 200 is called the vacuum UV because oxygen in the air absorbs strongly in this region. Measurements of sample absorption below 200 nm require specialized instrumentation that can purge oxygen from the light path to remove the interference.

UV-visible spectroscopy is commonly used for organic molecules but can also be used for light absorbing transition metal complexes and nanomaterials.

The selective absorption and transmittance of visible light and ultraviolet radiation are the basis of a spectroscopic technique for identifying compounds and for determining their concentrations in samples.

The Technique

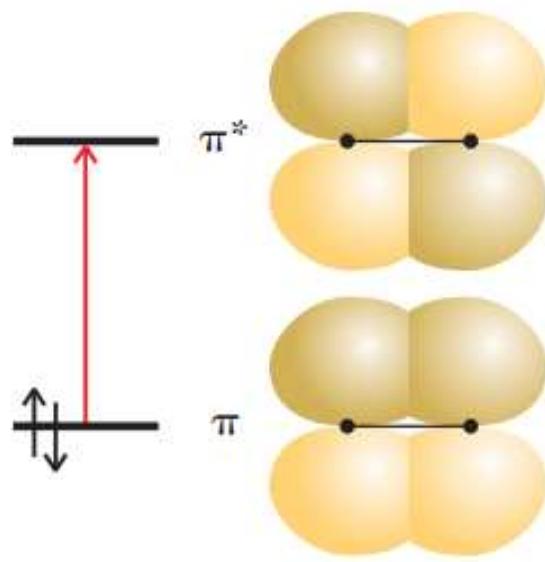
When electromagnetic radiation falls on a molecule, the electrons in the molecule can be excited to a higher energy state. Radiation of frequency ν (nu) can raise the energy of the molecule by an amount ΔE ,

$$\Delta E = h\nu \quad (1)$$

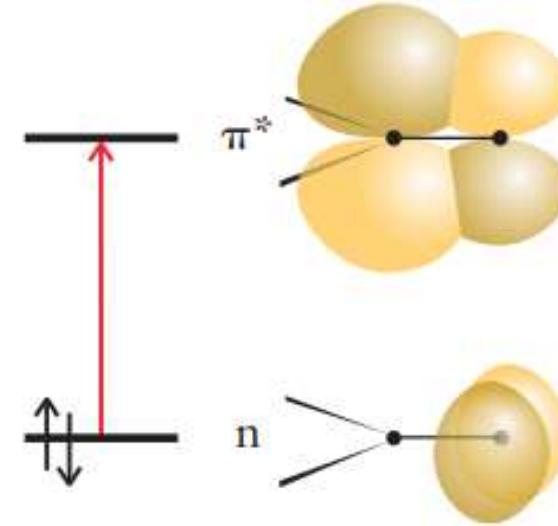
where h is Planck's constant. This equation is the Bohr frequency condition. Provided that an empty orbital exists at the right energy, the incoming radiation can excite an electron into it and hence be absorbed. For typical ultraviolet wavelengths (of 300 nm and less, corresponding to a frequency of about 10^{15} Hz), each photon brings enough energy to excite the electrons in a molecule into a different distribution. Therefore, the study of visible and ultraviolet absorption gives us information about the electronic energy levels of molecules.

Chromophores

Chromophores are the light absorbing moieties within a molecule. The presence of certain absorption bands in visible and ultraviolet spectra can often be traced to the presence of characteristic groups of atoms in the molecules. These groups of atoms are called chromophores, from the Greek words for “color bringer.” An important chromophore is a carbon–carbon double bond ($\text{C}=\text{C}$). Another important chromophore is the carbonyl group, $\text{C}=\text{O}$.



A π -to- π^* transition (e.g., in $\text{C}=\text{C}$): an electron in a bonding π orbital is excited into an empty antibonding π^* -orbital.



In an n -to- π^* transition ((e.g., in $\text{C}=\text{O}$, a carbonyl group), an electron in a nonbonding orbital (one localized wholly on the oxygen atom) is excited into an antibonding π^* -orbital spread over both atoms.

A d-metal ion may also be responsible for color, as is apparent from the varied colors of many d-metal complexes. Two types of transitions may be involved. In one, which is called a *d-to-d transition*, an electron is excited from a d-orbital of one energy to a d-orbital of higher energy. Because the energy differences between d-orbitals are quite small, visible light brings enough energy to cause this excitation, and so colors are absorbed from white light and the sample takes on colors complementary to those absorbed. In a second type of transition involving d-orbitals, called a charge-transfer transition, electrons migrate from the atoms attached to the central metal atom into the latter's d-orbitals or vice versa. This transfer of charge can result in very intense absorption; it is responsible, for instance, for the deep purple of permanganate ions, MnO_4^- .

Visible and ultraviolet absorption spectra are measured in an absorption spectrometer (Fig.1). The source gives out intense visible light or ultraviolet radiation. The wavelengths can be selected with a glass prism for visible light and with a quartz prism or a diffraction grating for ultraviolet radiation (which is absorbed by glass). The absorbed/transmitted as well as the incident light beams are sent to a photodetector, which measures the ratio of the **intensity of the reference beam (I_0)** to the **intensity of the sample beam (I)**. This is converted to the sample **absorbance ($A = \log (I_0/I)$)** for each wavelength by a data system and a plot of *absorbance versus wavelength*, called the *spectrum*, is recorded and displayed.

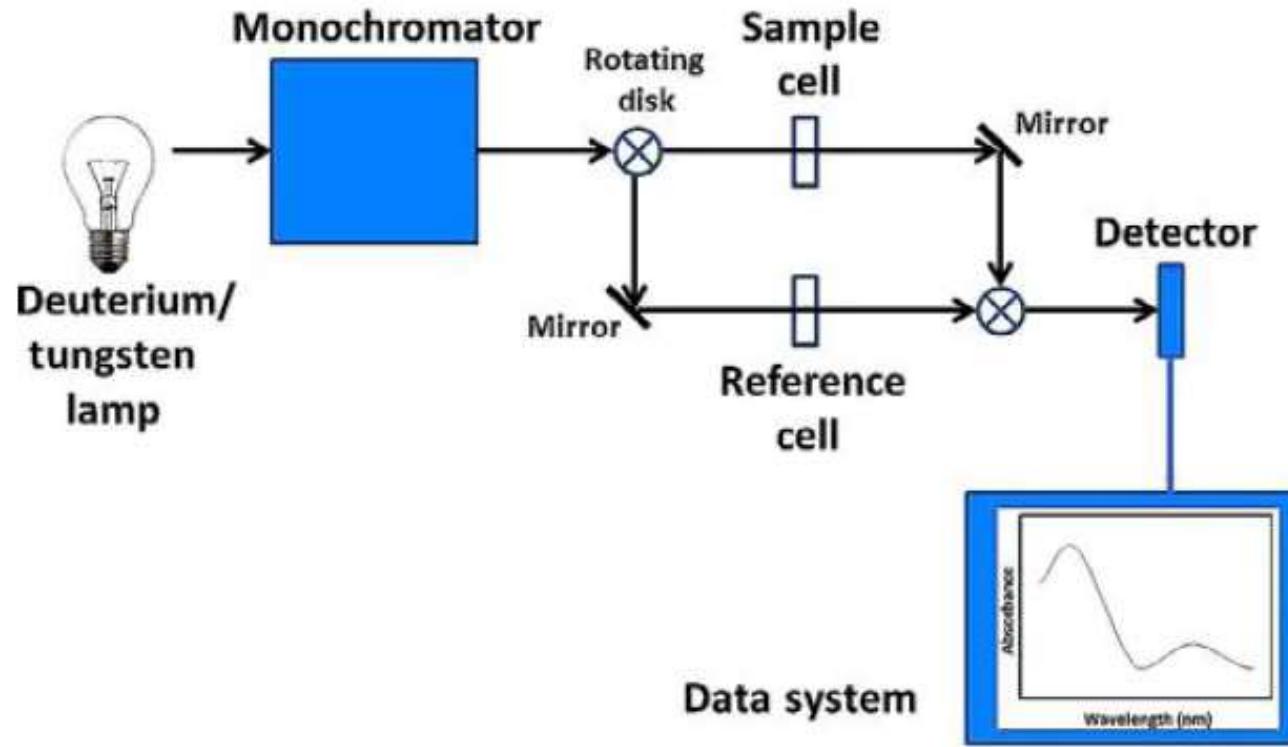


FIG 1. Schematic diagram of a double beam UV-visible absorption spectrometer.

A typical absorption spectrum, that of chlorophyll, is shown in Fig. 2. Note that chlorophyll absorbs red and blue light, leaving the green light present in white light to be reflected. That is why most vegetation looks green. The spectrum can help us to assess the absorption quantitatively and to make a precise analysis of the energy-capturing power of the molecule.

Unlike the atomic line spectra, molecular absorption spectra give broad bands with a measurable band width, as shown in Fig. 2. This is because, unlike atoms, molecules have vibrational energy levels that contribute to the ΔE between the electronic energy levels. A number of these molecular vibrational energy levels are available at each electronic energy level and transitions can occur between each of these vibrational levels. This results in a broadening of the absorption peak that occurs from the electronic transition. The more atoms there are in the molecule, the larger the number of molecular vibrational levels and the broader the absorption bands.

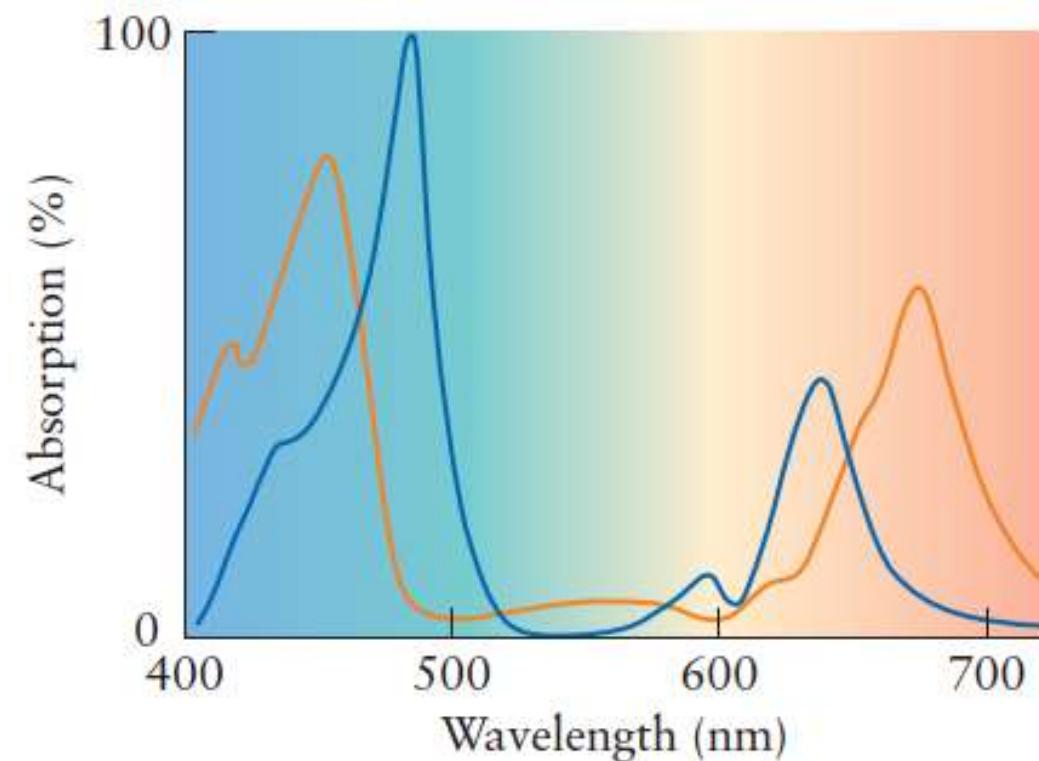


FIGURE 2 The optical absorption spectrum of chlorophyll as a plot of percentage absorption against wavelength. Chlorophyll a is shown in orange, and chlorophyll b in blue.

- The absorbance (A) is directly proportional to the concentration of the absorbing species and can be used to determine the amount of the species from the relationship known as Beer's Law, named for August Beer who discovered the relationship in 1852.
- Beer's Law for UV-visible absorption is written as;

$$A = \log (I_0/I) = \varepsilon c l$$

where ε is the molar absorptivity in units of $M^{-1} cm^{-1}$, c is the molar concentration (M), and l is the path length (cm).

- ε , the molar absorptivity, is the function of the wavelength.
- Although Beer's Law is followed at all wavelengths of an absorption band, it gives the best results at the wavelength of maximum absorption (λ_{max}).
- The molar absorptivity varies with the absorption across the band with ($\varepsilon = A/c/l$) and is also at a maximum value at λ_{max} , so the values for ε are always given at this wavelength.