

Valence bond theory

The valence bond theory was developed by Professor Linus Pauling, of the California Institute of Technology, and made available in his excellent book, *The Nature of the Chemical Bond*, published in 1940, 1948, and 1960. Along with the late Marie Curie, Professor Pauling is one of the very few persons to have been awarded two Nobel prizes, the Nobel prize in chemistry in 1954 and the Nobel peace prize in 1962. Pauling's ideas have had an important impact on all areas of chemistry; his valence bond theory has aided coordination chemists and has been extensively used. It can account reasonably well for the structure and magnetic properties of metal complexes. Extensions of the theory will account for other properties of coordination compounds such as absorption spectra, but other theories seem to do this more simply. Therefore, in recent years coordination chemists have favored the crystal field, ligand field, and molecular orbital theories. It is useful to show the valence bond representations of the complexes $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$, which can then be compared with representations from the crystal field and molecular orbital theories to be discussed later. First, we must know from experiment that $[\text{CoF}_6]^{3-}$ contains four unpaired electrons, whereas $[\text{Co}(\text{NH}_3)_6]^{3+}$ has all of its electrons paired. Each of the ligands, as Lewis bases, contributes a pair of electrons to form a coordinate covalent bond. The valence bond theory designations of the electronic structures are shown in Figure 2.7. The bonding is described as being covalent. Appropriate combinations of metal atomic orbitals are blended together to give a new set of orbitals, called hybrid orbitals. In six-coordinated systems, the hybrid orbitals involve the s , p_x , p_y , p_z , $d_{x^2-y^2}$, and d_{z^2} atomic orbitals. The resulting six sp^3d^2 or d^2sp^3 hybrid orbitals point toward corners of an octahedron. For $[\text{CoF}_6]^{3-}$ the orbitals used have the same principal energy level as the s and p orbitals. A complex of the $nsnp^3nd^2$ type is called an outer-orbital complex because it uses "outer" d

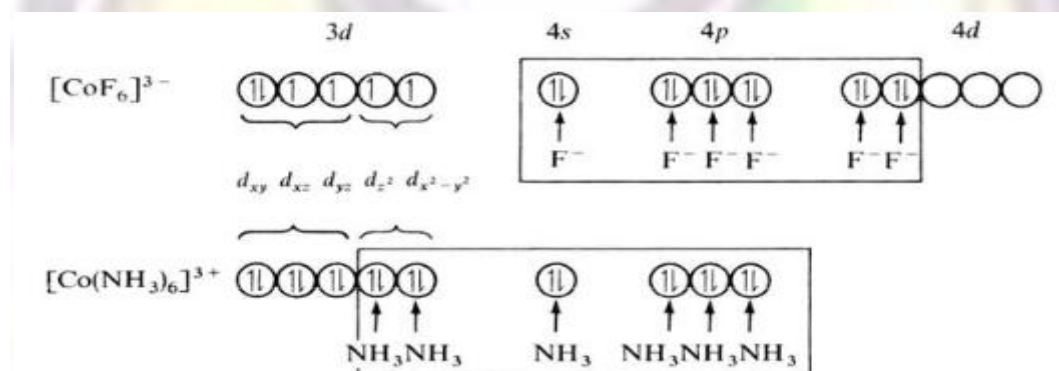


Figure 2.7 Valence bond theory representations of $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$.

orbitals. On the other hand, $[\text{Co}(\text{NH}_3)_6]^{3+}$ uses orbitals of a lower principal energy level than the sand orbitals. Such a complex, $(n - 1)d_2nsnp_3$, is called an inner-orbital complex because it uses "inner" orbitals. See Section 2.5 for nomenclature used in these systems on the basis of the crystal field theory .

Crystal field theory

Crystal field theory (CFT) has been widely used by chemists to explain the behavior of transition metal compounds. Although the more general ligand field and molecular orbital theories are more extensively used, the basic ideas of crystal field theory are still useful and provide a convenient bridge for understanding the more complicated theories. In direct contrast with valence bond theory (VBT), which is essentially a theory for covalent bonding, CFT is an ionic model. Metal ligand bonds are described as resulting from the attraction of positive metal ions for negatively charged ligands (or the negative end of uncharged but polar ligands). In CFT, covalent interactions are totally neglected. The greatest barrier to understanding CFT is frequently the inability of people to exclude covalent concepts such as electron pair bonds and overlapping orbitals from their thinking. Calculations of coordinate bond energies can be made using classical potential energy equations that take into account the attractive and repulsive interactions between charged particles (10)

$$\text{bond energy} \propto \frac{q_1 q_2}{r}$$

q_1 and q_2 are charges on the interacting ions and r is the distance that separates ion centers. A similar equation applies to the interaction between an uncharged polar molecule and an ion. This approach gives results that are in reasonably good agreement with experimental bond energies for non-transition-metal complexes. For transition-metal complexes calculated values are often too small. This discrepancy is largely corrected when orbital electrons are considered and allowance is made for the effect of ligands on the relative energies of orbitals. This refinement of electrostatic theory was first recognized and used by the physicists Bethe and Van Vleck in 1930 to explain colors and magnetic properties of crystalline solids. Their theory known as crystal field theory was proposed at about the same time as—or even a little earlier than—VBT, but it took about twenty years for the CFT to be recognized and used by chemists. Perhaps this was because CFT was written for physicists and VBT gave such a satisfying pictorial representation of the bonded atoms. In 1951, several theoretical chemists working independently used CFT to interpret spectra of transition-metal complexes with such success that there followed an immediate avalanche of research activity in the area. It soon

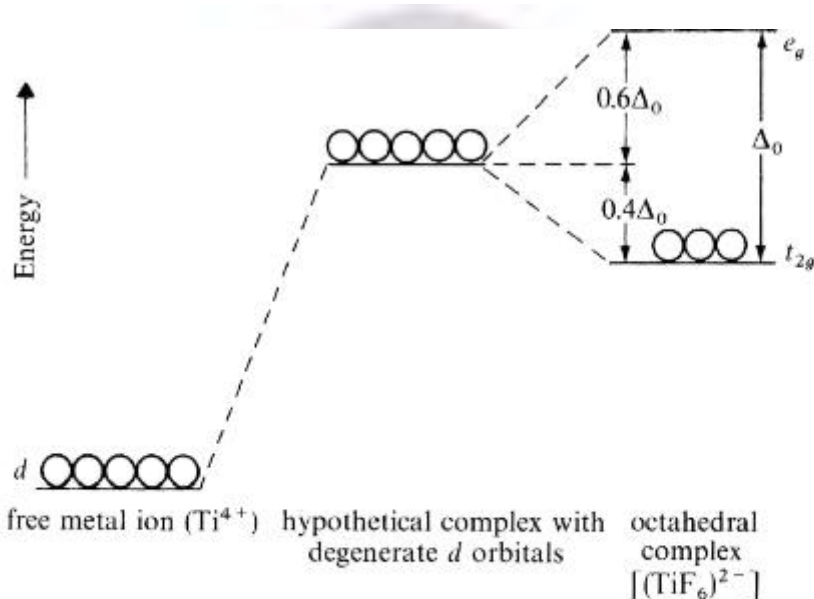
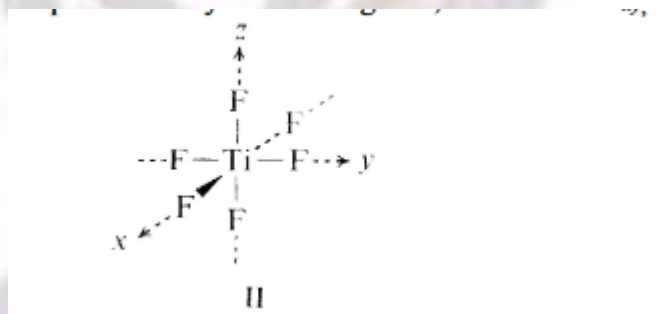


Figure 2.8 The energies of the d orbitals in a free metal ion, in a hypothetical complex in which there is no crystal field splitting, and in an octahedral complex.

became apparent that CFT could explain in a semiquantitative fashion many of the properties of coordination compounds. To understand CFT, it is necessary to have a clear mental picture of the spatial orientation of d orbitals (Figure 2.6). It is the interaction of the d orbitals of a transition metal with ligands surrounding the metal that produces crystal field effects. We can illustrate CFT by considering the octahedral complex $[TiF_6]^{2-}$. In a free Ti^{4+} ion, one isolated from all other species, the electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6$; no d electrons are present. The five empty 3d orbitals of this ion have identical energies. This means that an electron may be placed in any one of these d orbitals with equal ease. Orbitals that have the same energy are called degenerate orbitals. In $[TiF_6]^{2-}$, the Ti^{4+} ion is surrounded by six F^- ions. These F^- ions make it much more difficult to place electrons in the Ti^{4+} d orbitals due to repulsion of the electrons by the negative charge on F^- ions. In other words, the energy of the d orbitals increases as F^- ions (or other ligands) approach the orbitals (Figure 2.8).

If the six F^- ions surrounding Ti^{4+} in $[TiF_6]^{2-}$ were situated equally near each of the five d orbitals of Ti^{4+} , all of these orbitals would have the same energy (they would be degenerate), but an energy considerably greater than that which they had in the free Ti^{4+} ion. However, an octahedral complex in which all orbitals remain degenerate is but a hypothetical situation. The complex $[TiF_6]^{2-}$ has an octahedral structure; for convenience, we shall visualize this complex with the six F^- ions residing on the x , y , and z axes of a cartesian coordinate system (structure II). In this orientation, F^- ions are very near the $d_{x^2-y^2}$ and d_{z^2} orbitals, which are referred to as e_g orbitals (Figure 2.8).

These e_g orbitals point directly at the F^- ligands, whereas the d_{xy} , d_{xz} , and



d_{yz} orbitals—called t_{2g} orbitals—point between the ligands. Therefore, it is more difficult to place electrons in e_g orbitals than in t_{2g} orbitals, which means that e_g orbitals are of higher energy than t_{2g} orbitals. This conversion of the five degenerate orbitals of the free metal ion into groups of orbitals having different energies is the primary feature of CFT; it is known as CF splitting. As we have seen, splitting results because orbitals have a certain orientation in space and because neighboring atoms, ions, or molecules can change the energy of orbitals that are directed toward them in space. Many students find CFT and its concept of crystal field splitting difficult to visualize. The preceding discussion attempts to describe the essential concepts in simple terms on the basis of the spatial geometries of the orbitals. This is the correct approach to CFT. It may, however, be helpful to develop a simple physical picture of crystal field splitting. Refer to Figure 2.9 and imagine that the metal ion with its electron cloud can be represented by a sponge ball. Now consider what happens when a rigid spherical shell (corresponding to ligands) is forced around the outside of the ball. The volume of the ball decreases, and the system has a higher energy, as is evident from the fact that the sponge will expand spontaneously to its original volume upon removal of the constricting shell. This change in energy corresponds to the increase in energy that

results 1 The symbols e_g and t_{2g} are terms used in the mathematical theory of groups. The t_{2g} refers to a triply degenerate set of orbitals; the e_g , a doubly degenerate set

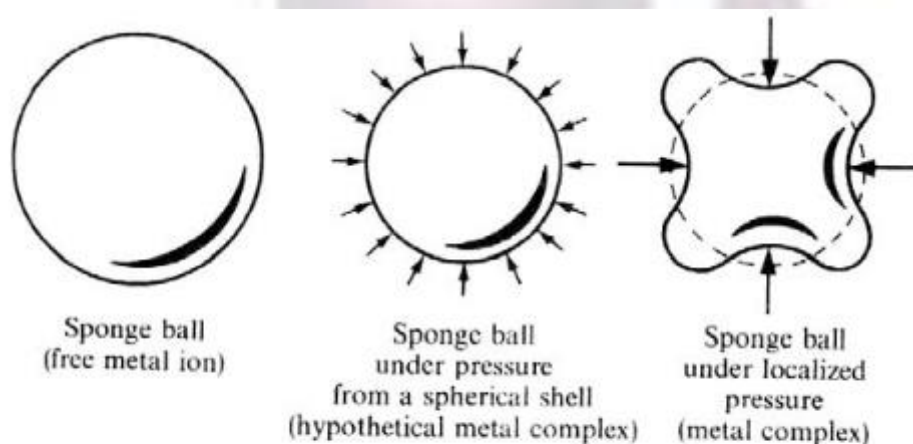


Figure 2.9 Crystal field effects visualized as a sponge ball under spherical pressure and under localized pressure. Compare with Figure 2.8.

from repulsion between electrons in a metal ion and electrons of ligands in the hypothetical complex (Figure 2.8). Now if the rigid shell is allowed instead to concentrate its total force on six particular spots (for example, the corners of an octahedron), then the sponge is pressed inward at these positions but bulges outward between them. Compared with the spherically constricted system, the sponge at the six points of high pressure is at a higher energy and at the bulges between is at a lower energy. This corresponds to crystal field splitting with bulges related to t_{2g} orbitals and points of depression related to e_g orbitals. In the preceding discussion, it was noted that the energy of the orbitals of a metal ion increases when ligands approach the ion. This, in itself, suggests that a complex should be less stable than a free metal ion. However, the fact that complexes do form indicates that the complex is a lower energy configuration than the separated metal ion and ligands. The increase in energy of the orbitals of the metal ion is more than compensated for by the bonding between metal ion and ligand. In the case of $[\text{TiF}_6]^{2-}$, bonding can be visualized as the result of electrostatic attraction between negative fluoride ions and the positive titanium ion. In an octahedral arrangement of ligands, the t_{2g} and e_g sets of orbitals have different energies. The energy separation between them is given the symbol Δ_o . It can be proved for an octahedral system that the energy of t_{2g} orbitals is $0.4\Delta_o$ less than that of the five hypothetical degenerate orbitals that result if crystal field splitting is neglected (Figure 2.8). Therefore, the e_g orbitals are $0.6\Delta_o$ higher in energy than the hypothetical degenerate orbitals. In an octahedral complex that contains

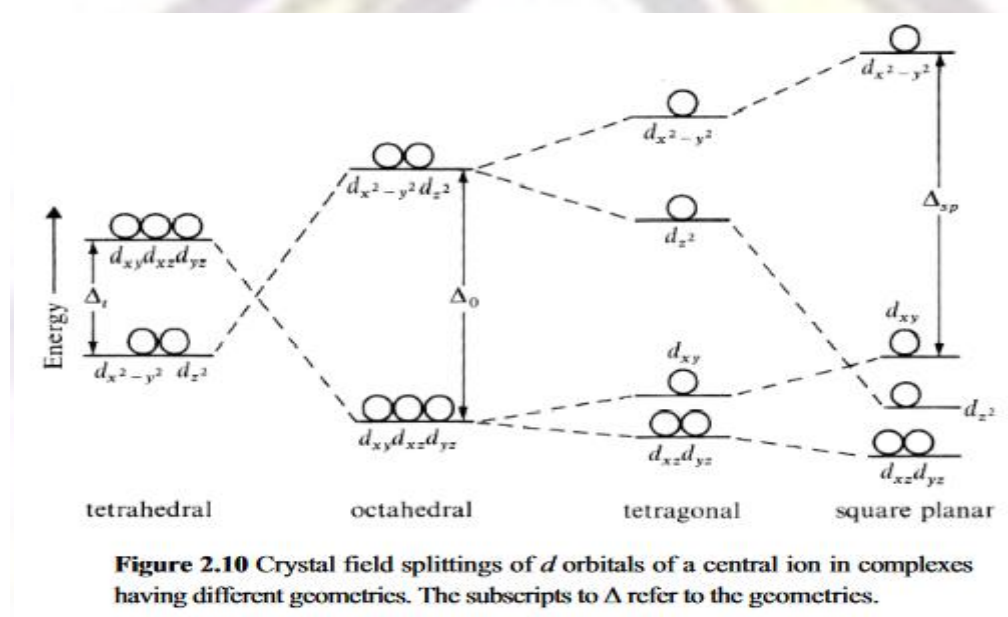
one d electron (for example, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$) that electron will reside in the orbital of lowest energy. Simple electrostatics does not recognize that orbitals in a complex have different energies. Therefore, theory predicts that the d electron would have the energy of the hypothetical degenerate orbitals. In fact, the d electron goes into a t_{2g} orbital that has an energy $0.4\Delta_o$ less than that of the hypothetical degenerate orbitals. Thus the complex will be $0.4\Delta_o$ more stable than the simple electrostatic model predicts. In simple terms, we can say that the d electron, and hence the whole complex, has a lower energy as a result of the placement of the electron in a t_{2g} d orbital that is as far from the ligands as possible. The $0.4\Delta_o$ is called the crystal field stabilization energy (CFSE) for the complex. Table 2.1 gives CFSE's for metal ions in octahedral complexes. The values in Table 2.1 are readily calculated by assigning a value of $0.4\Delta_o$ for each electron put in a t_{2g} orbital and a value of $-0.6\Delta_o$ for each electron put in an e_g orbital. Thus, the CFSE for a d_5 system is either $3(0.4\Delta_o) + 2(-0.6\Delta_o) = 0.0\Delta_o$ or $5(0.4\Delta_o) + 0(-0.6\Delta_o) = 2.0\Delta_o$, depending on the distribution of the five electrons in the t_{2g} and e_g orbitals. Simple electrostatics treats a metal ion as a spherical electron cloud surrounding an atomic nucleus. CFT provides a better model, since it admits that d electrons provide a nonspherical electron cloud in order to avoid positions in which ligands reside. (They provide a nonspherical electron cloud

Table 2.1 Crystal field stabilization energies for metal ions in octahedral complexes

<i>d</i> electrons in metal ions	Stabilization, Δ_o			Stabilization, Δ_o		
	t_{2g}	e_g		t_{2g}	e_g	
1	↑ ○ ○	○ ○	0.4			
2	↑ ↑ ○	○ ○	0.8			
3	↑ ↑ ↑	○ ○	1.2			
4	↑ ↑ ↑	↑ ○	0.6	↑ ↑ ↑	○ ○	1.6
5	↑ ↑ ↑	↑ ↑	0.0	↑ ↑ ↑	○ ○	2.0
6	↑ ↑ ↑	↑ ↑	0.4	↑ ↑ ↑	○ ○	2.4
7	↑ ↑ ↑	↑ ↑	0.8	↑ ↑ ↑	↑ ○	1.8
8	↑ ↑ ↑	↑ ↑	1.2			
9	↑ ↑ ↑	↑ ↑	0.6			
10	↑ ↑ ↑	↑ ↑	0.0			

by residing preferentially in low-energy orbitals that point between ligands.) Therefore, CFT explains why simple electrostatic calculations consistently underestimate the stability of transition-metal complexes and compounds; the simple approach neglects the nonspherical electron distribution and the resulting CFSE. An early objection to a simple electrostatic treatment of

bonding for metal complexes was that it could not explain the formation of square planar complexes. It was argued that if four negative charges are held to a positive central ion by electrostatic forces alone, then the negative charges must be at corners of a tetrahedron. Only in such a structure can negative groups attain maximum separation and so experience a minimum electrostatic repulsion. This is correct if the central ion is spherically symmetric. However, such symmetry is not typical of transition-metal ions, because electrons will reside in low-energy orbitals that point between ligands and do not have spherical symmetry. In Section 3.1 it is shown that CFT can account for square planar complexes and that it predicts the distortion of certain octahedral complexes. We have considered the crystal field splitting for octahedral complexes; now let us consider complexes of other geometries. It is convenient to start with the crystal field splitting for an octahedral structure and consider how the splitting is affected by a change in geometry (Figure 2.10). In going from a regular octahedron to a square planar structure, the effect amounts to removal of any two trans ligands from the octahedron. Generally, we speak of the xy plane as the square plane, which means trans groups are removed from the z axis. If ligands on the z axis are moved out so that the metal–ligand distance is only slightly greater than it is for the four ligands in the xy plane, the result is a tetragonal structure (Figure 2.10). This permits ligands in the xy plane to



approach the central ion more closely. Consequently, orbitals in the xy plane experience a greater repulsion from ligands than they do in an octahedral structure, and we find an increase in energy of the $d_{x^2-y^2}$ and d_{xy} orbitals (Figure 2.10). At the same time orbitals along the z axis or in the xz and yz plane experience a smaller repulsion from ligands, which are now some distance removed along the z axis. This results in a sizable decrease in energy for d_{z^2} orbital and a slight decrease for d_{xz} and

d_{yz} orbitals, relative to the octahedral arrangement. The same splitting pattern is found for a square pyramidal structure, in which there is one ligand on the z axis and the other four ligands plus the central atom are in the xy plane. The complete removal of two ligands on the z axis to give a square planar configuration is then accompanied by a further increase in energy of the $d_{x^2-y^2}$ and d_{xy} orbitals, as well as a further decrease for the d_{z^2} , d_{xz} , and d_{yz} orbitals. The crystal field splitting of orbitals for a tetrahedral structure is more difficult to visualize. We must first try to picture a tetrahedron placed inside a cube (Figure 2.11). The four corners of the tetrahedron are then located at four of the corners of the cube. If we now insert $x, y,$ and z axes so they go through the center of the cube and protrude from the centers of its six faces, we can begin to see the position of the four ligands with respect to the orbitals of the central atom. The orbitals along the cartesian axes ($d_{x^2-y^2}$ and d_{z^2}) are further removed from the four ligands than are orbitals between the axes (d_{xy} , d_{xz} , and d_{yz}). Therefore, e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) are the low-energy orbitals in

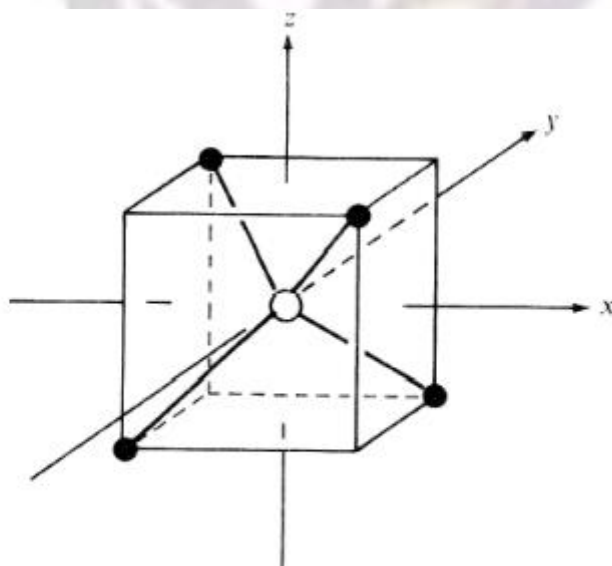


Figure 2.11 A tetrahedral complex with its center at the center of a cube.

tetrahedral complexes; t_{2g} orbitals (d_{xy} , d_{xz} , d_{yz}) are of relatively higher energy. It has been observed that the energy separation between e_g and t_{2g} orbitals, the crystal field splitting Δ_t , is only about one-half of Δ_o . Hence, crystal field effects favor the formation of octahedral complexes over that of tetrahedral complexes. Magnetic properties The magnetic properties of transition-metal complexes can readily be understood in terms of CFT. Transition metal ions have partially filled orbitals. If these orbitals are degenerate, Hund's rule predicts that unpaired electrons will be present. For example, a metal ion containing three d electrons (called a d_3 system) should have three unpaired electrons a d_8 metal ion should have two unpaired electrons and three pairs of electrons). Materials that contain unpaired electrons are attracted to a magnet and are said to be paramagnetic. (This attraction is much weaker than that exhibited by ferromagnetic materials such as iron.) The magnitude of attraction of a material to a magnet is a measure of the number of unpaired electrons present. Paramagnetism can be measured with a relatively simple device called a Gouy

balance. The sample is placed in a tube suspended from a balance, and the weight of the sample is measured both in the presence and in the absence of a magnetic field. If the material is paramagnetic, it will weigh more while the magnetic field is present and attracting it. The increase in weight is a measure of the number of unpaired electrons in the compound. A gaseous Co^{3+} ion, a d^6 system, has five degenerate orbitals and is expected to have four unpaired electrons. However, some d^6 cobalt(III)



complexes such as $[\text{Co}(\text{NH}_3)_6]^{3+}$ are not attracted to a magnet (they are diamagnetic). Complexes in which some of the unpaired electrons of the gaseous metal ion have been forced to pair are called low-spin complexes. The cobalt(III) complex $[\text{CoF}_6]^{3-}$ is paramagnetic and contains four unpaired electrons. It is an example of a high-spin complex. The electron distributions for these two complexes can be represented as , respectively. A variety of names have been given to the behavior for which we have used the terms “high-spin” and “low-spin”. These are summarized below. It is now necessary to try to understand why in such systems orbital electrons are distributed differently. It must be recognized that at least two effects determine the electron distribution. First, the normal tendency is for electrons to remain unpaired. Energy sufficient to overcome the repulsive interaction of two electrons occupying the same orbital is required to cause pairing. Second, in the presence of a crystal field, orbital electrons will tend to occupy low-energy orbitals and thus avoid, as much as possible, repulsive interaction with ligands. If the stability thus gained (Δ) is large enough to overcome the loss in stability due to electron pairing, then electrons couple and the result is a low-spin complex. Whenever the crystal field splitting (Δ) is not sufficient, electrons remain unpaired and the complex is a high-spin type. Note in Figure 2.12 that the value of Δ_o for $[\text{CoF}_6]^{3-}$ is smaller than that for $[\text{Co}(\text{NH}_3)_6]^{3+}$. Complexes in which Δ is large will generally be low-spin complexes. Additional examples of crystal field splitting and electron distributions in metal complexes are shown in Figure 2.13.

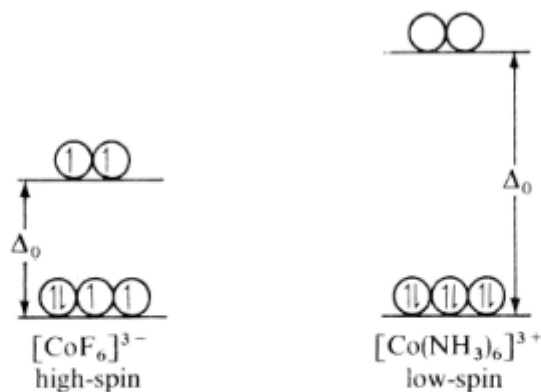


Figure 2.12 Relative crystal field splittings (Δ_0) of the d orbitals in high-spin and low-spin octahedral cobalt(III) complexes.

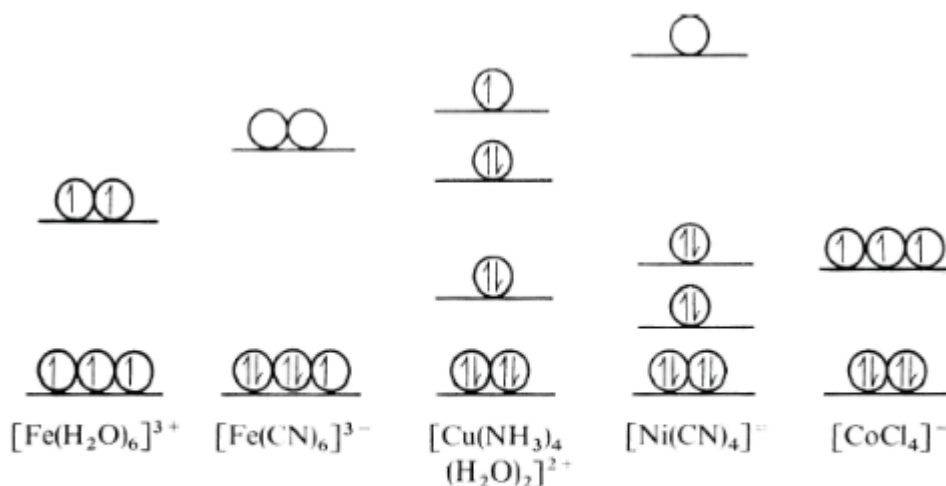
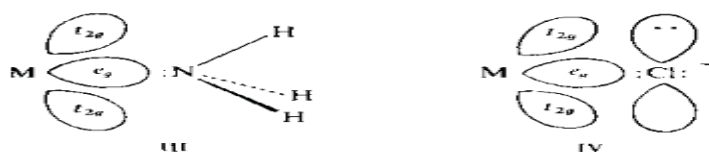


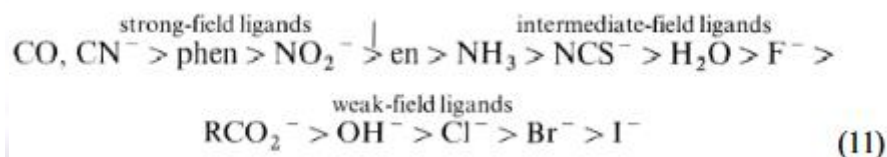
Figure 2.13 Crystal field splittings and electron distributions for some metal complexes. The structures of the first two complexes are octahedral, and the others (left to right) are tetragonal, square planar, and tetrahedral (see Figure 2.10).

The magnitude of the crystal field splitting determines whether electrons in a metal ion will pair up. It also influences a variety of other properties of transition metals. The extent of the crystal field splitting depends on several factors. The nature of the groups (ligands) providing the crystal field is of greatest interest. From an electrostatic point of view, ligands with a large negative charge and those that can approach the metal closely (small ions) should provide the greatest crystal field splitting. Small, highly charged ions will make any orbital they approach an energetically unfavorable place to put an electron. This reasoning is in agreement

with the observation that the small F⁻ causes a greater crystal field splitting than the larger halide ions Cl⁻, Br⁻, and I⁻. Since crystal field splitting arises from a strong interaction of ligands with orbitals that point directly toward them and a weak interaction with those that point between, in order to achieve a large crystal field splitting it is desirable that a ligand "focus" its negative charge on an orbital. A ligand with one free electron pair (for example, NH₃) can be visualized as doing this much more readily than a species with two or more free electron pairs, see structures III and IV. This type of argument can be used to account for the observation



that neutral NH₃ molecules cause a greater crystal field splitting than H₂O molecules or negatively charged halide ions. In general, however, it is difficult to explain the observed ability of various ligands to cause crystal field splitting with a simple electrostatic model. The crystal field splitting ability of ligands has been observed to decrease in the order (11). To account for this order, it is necessary to abandon a completely



ionic electrostatic model for the bonding in complexes and to realize that covalent interactions also exist. A modified CFT that includes the possibility of covalent bonding is called ligand field theory. It can account, at least qualitatively, for the crystal field splitting caused by various ligands. Molecules such as CO, CN⁻, phen, and NO₂⁻, which provide the largest crystal fields, are all able to form Δ bonds with the central metal atom (Section 2.6). This Δ bonding can markedly increase the magnitude of the crystal field splitting. The crystal field splitting is also strongly influenced by the oxidation state of the metal ion and the type of d electrons present. In general, the higher the oxidation state of the metal ion, the larger will be the crystal field splitting. The complex [Co(NH₃)₆]³⁺ is a diamagnetic low-spin complex, whereas [Co(NH₃)₆]²⁺ is a paramagnetic high-spin complex. The crystal field splitting in the cobalt(III) complex is about twice as great as in the cobalt(II) complex; this results in pairing of electrons. One can attribute the larger Δ_o for cobalt(III) to the fact that ligands can approach more closely the slightly smaller, higher-charged metal ion and hence interact more strongly with its d orbitals. The

crystal field splitting in $[\text{Rh}(\text{NH}_3)_6]^{3+}$ and $[\text{Ir}(\text{NH}_3)_6]^{3+}$ is greater than in $[\text{Co}(\text{NH}_3)_6]^{3+}$. In general, the crystal field splitting is greatest for complexes containing 5 d electrons and least for those containing 3 d electrons. One might attribute this behavior to the fact that 5 d orbitals extend farther into space and thus interact more strongly with ligands.

Colors of transition metal ions

The greatest achievement of CFT is its success in interpreting colors of transition-metal compounds. One consequence of the comparatively small energy differences Δ between nonequivalent d orbitals in transition-metal complexes is that excitation of an electron from a lower to a higher level can be achieved by absorption of visible light. This causes the complex to appear colored. For example, an aqueous solution of titanium(III) is violet. The color is an indication of the absorption spectrum of the complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ (Figure 2.14). That the complex absorbs light in the visible region is explained by the electronic transition of the t_{2g} electron into an e_g orbital (Figure 2.15).

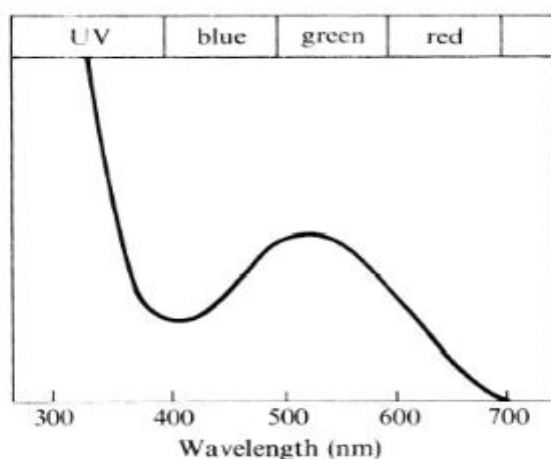


Figure 2.14 The absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. Solutions of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ are red-violet because they absorb green light but transmit blue and red.

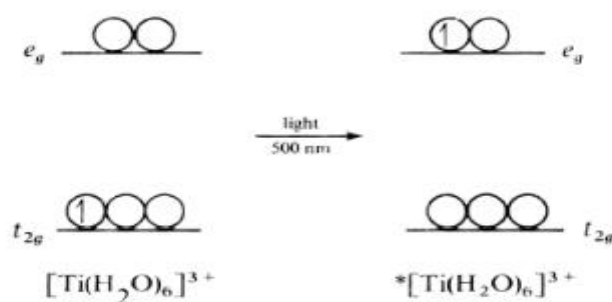


Figure 2.15 The $d-d$ electronic transition responsible for the violet color of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$.

Absorption spectra of complexes containing more than one d electron are more complicated because a greater number of electronic transitions are possible. Planck's equation (12) relates the energy E of an electronic transition to the wavelength λ of the light absorbed; h is Planck's constant (6.63×10^{-34} J-s),

$$E = \frac{hc}{\lambda} \quad (12)$$

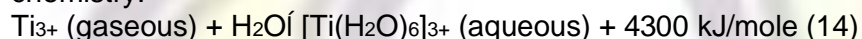
and c is the speed of light (3.00×10^8 m/s). The units of E are joules/molecule and of λ , meters. From equation (12) it is possible to determine the energy difference Δ between orbitals that are involved in the electronic transition.

Collection

of the constants h and c plus the use of Avogadro's number, 6.02×10^{23} molecules/mole, gives us equation (13). E has the units kilojoules/mole and λ

$$E = \frac{1.20 \times 10^5}{\lambda} \quad (13)$$

is in nanometers. The maximum in the visible absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is found at a wavelength of 500 nm, giving us a value of 240 kJ/mole for the energy difference between t_{2g} and e_g orbitals. The crystal field splitting Δ_o of 240 kJ is of the same order of magnitude as many bond energies. Although this value of 240 kJ is small compared to the heat of hydration of Ti^{3+} (14), 4300 kJ/mole, the crystal field splitting is very important and necessary to an understanding of transition-metal chemistry.

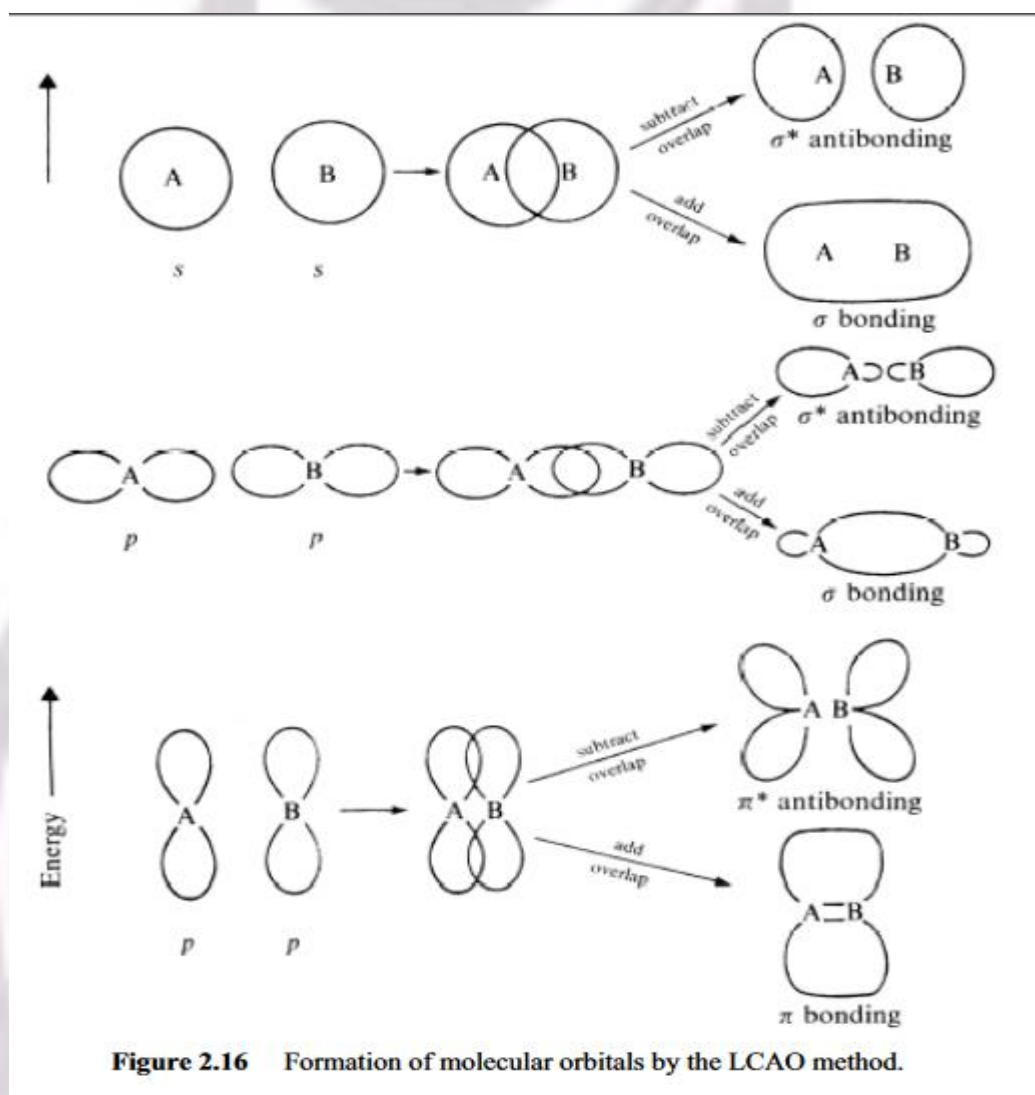


Note that the simple ionic model that is the basis of CFT does not accurately represent bonding in transition-metal compounds. There is ample experimental evidence that both ionic and covalent bonding play an important role. Nonetheless, the ionic CFT provides a simple model that will explain a great deal of transition-metal behavior and, moreover, one that has led and will lead to the formulation of many instructive experiments. The role of CFT in the structure, stability, and reactivity of complexes is discussed later.

Molecular orbital theory

The molecular orbital theory (MOT) is widely used by chemists. It includes both the covalent and ionic character of chemical bonds, although it does not specifically mention either. MOT treats the electron distribution in molecules in very much the same way that modern atomic theory treats the electron distribution in atoms. First, the positions of atomic nuclei are determined. Then orbitals around nuclei are defined; these molecular orbitals (MO's) locate the region in space in which an electron in a given orbital is most likely to be found. Rather than being localized around a single atom, these MO's extend over part or all of the molecule. Since calculation of MO's from first principles is difficult, the usual approximate approach is the linear combination of atomic orbitals (LCAO) method. It seems reasonable that MO's of a molecule should resemble atomic orbitals (AO's) of the atoms of which the molecule is composed. From known shapes of AO's, one can approximate shapes of

MO's. The linear combinations (additions and subtractions) of two atomic orbitals to give two molecular orbitals are pictured in Figure 2.16. One MO results from addition of the parts of AO's that overlap, the other from their subtraction. The MO that results from addition of two orbitals includes the region in space between the two nuclei; it is called a bonding MO, and is of lower energy



than either of the two sAO's from which it arose. The MO that results from subtraction of the parts of AO's that overlap does not include the region in space between the nuclei. It has a greater energy than the original AO's, and it is called an antibonding MO. The energy difference between bonding and antibonding MO's can be appreciated if one realizes that electrons, when they reside in a region between two

nuclei, are strongly attracted by both nuclei. Combinations of atomic orbitals give σ (sigma) MO's. A combination of pAO's, as shown in Figure 2.16, may give either σ or π (π) MO's. In a σ MO, there is a plane passing through both nuclei along which the probability of

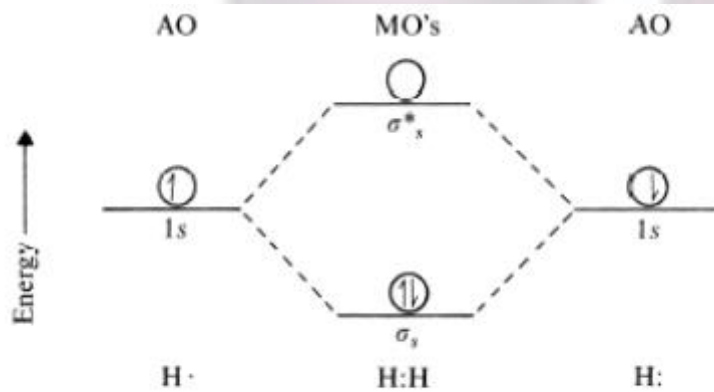


Figure 2.17 Molecular orbital diagram for the hydrogen molecule.

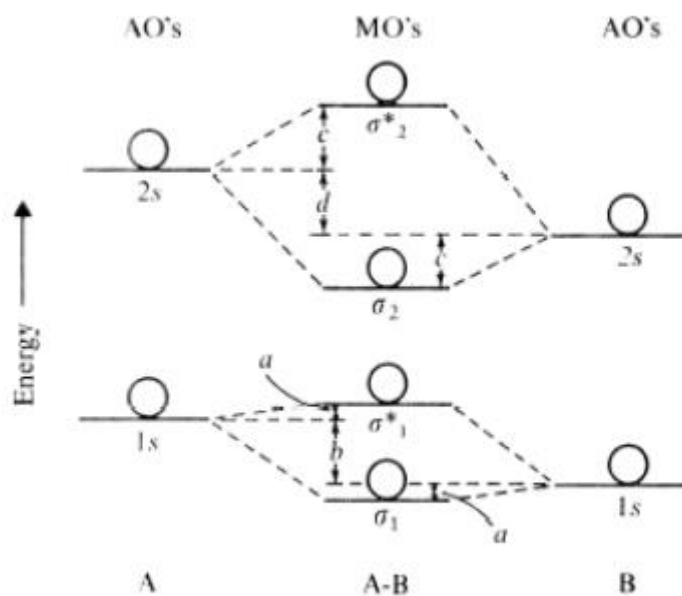


Figure 2.19 Molecular orbital diagram for an AB molecule.

finding an electron is zero. Electrons in π MO's reside only above and below the bond axis. To illustrate the use of MOT, let us look at MO energy diagrams for a few simple molecules. The H_2 molecule diagram is shown in Figure 2.17. In separated H atoms, one electron resides in each hydrogen AO. In the H_2 molecule, both electrons reside in the low-energy σ -bonding MO. The H_2 molecule is more stable than the separated H atoms; the two electrons are both in a lower-energy orbital in the molecule. The difference between the energy of the AO's and the bonding MO depends on how much the AO's overlap in the molecule. A large overlap results in a large difference and hence a strong bond; a small overlap results in a small difference, and hence the molecule will be of only slightly lower energy than the separated atoms. The dihelium ion He_2^+ is a three-electron system; its MO energy level diagram is shown in Figure 2.18. Since an orbital can hold only two electrons, the third electron must go in the σ^* antibonding MO. This orbital is of higher energy than the AO's of separated He atoms; thus placing an electron in the σ^* MO represents a loss of energy and results in a less stable system. This is in agreement with the experimental observation that the He_2^+ bond energy is

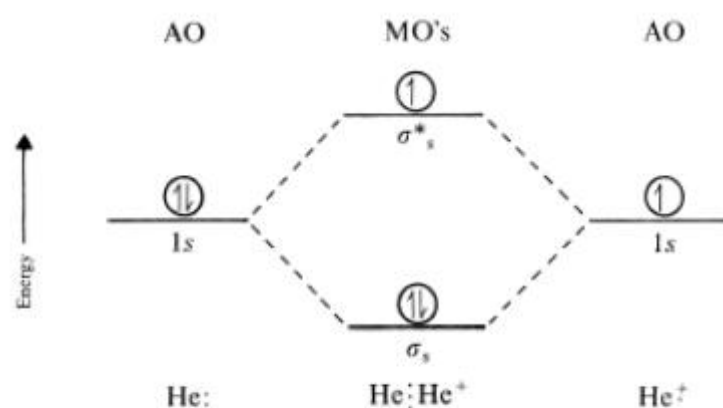


Figure 2.18 Molecular orbital diagram for the dihelium ion.

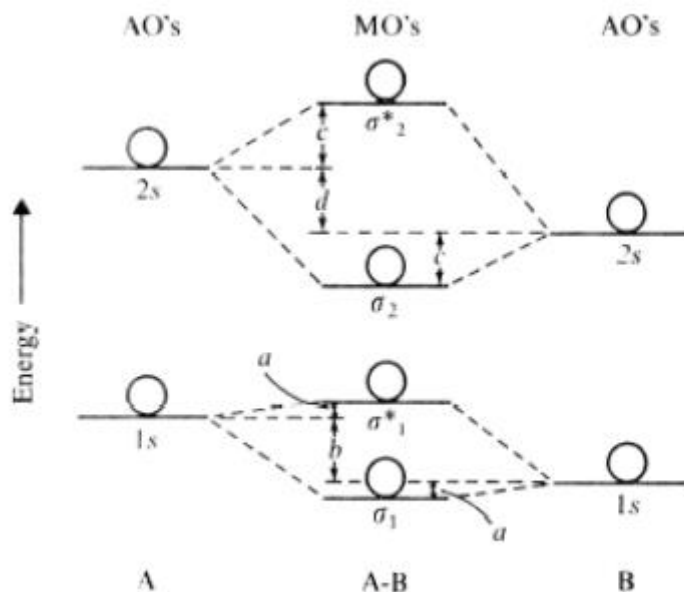


Figure 2.19 Molecular orbital diagram for an AB molecule.

only 238 kJ/mole compared with 436 kJ/mole for H₂. The four-electron He₂ molecule would be no more stable than two free He atoms. A MO energy level diagram for the general molecule AB is shown in Figure 2.19. There are an infinite number of higher-energy MO's for the AB molecule just as there are an infinite number of higher-energy AO's for the A and B atoms, but the orbitals of interest are low-energy orbitals in which electrons reside. When two different types of atoms are present, the energies of the AO's are expected to differ (for example, 1s orbitals of A and B have different energies). The more electronegative element will have the lowest-energy AO's. The difference in energy between AO's of two elements (Figure 2.19b and d) is a measure of the amount of ionic character in the bond. In H₂, 1s orbitals of the two H atoms have the same energy; hence there is no ionic character in the bond. The MO energy level diagrams for metal complexes are much more complicated than those for simple diatomic molecules. However, in the MO diagrams for [Co(NH₃)₆]³⁺ and [CoF₆]³⁺ in Figure 2.20 one can recognize several familiar features. On the left are 3d, 4s and 4p atomic orbitals of Co³⁺. The lower- and higher-energy AO's are of less interest. Since six ligands are involved, the right side of the diagram is somewhat different from diagrams we have seen previously. Only one orbital from each ligand, that used in σ bonding, is shown. (More complicated diagrams are sometimes used.) Since all six ligands are alike, the six ligand orbitals all have the same energy. Ligand orbitals are, in general, of lower energy than the metal orbitals, and hence the bonds have some ionic character. Bonding MO's, in general, are closer in energy to ligand orbitals than to metal orbitals and are more like the ligand orbitals; placing metal electrons in these MO's thus transfers electronic charge from metal to ligands. Two d orbitals (the e_g orbitals, d_{x²-y²} and d_{z²}), 40 Coordination chemistry

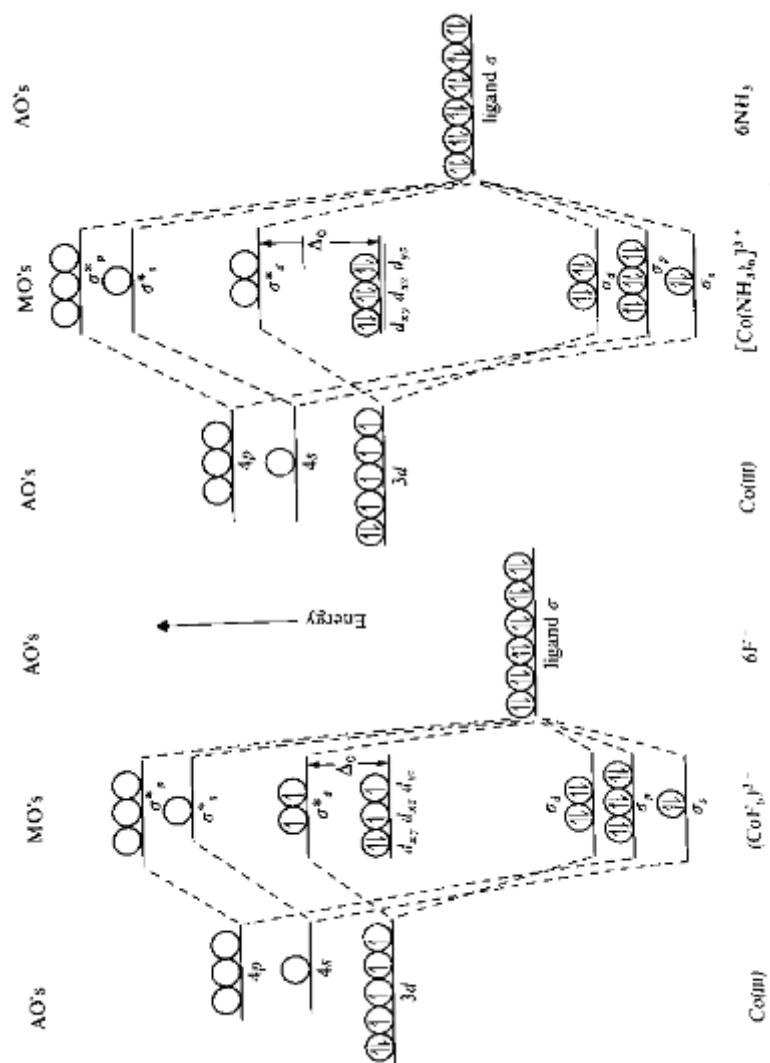
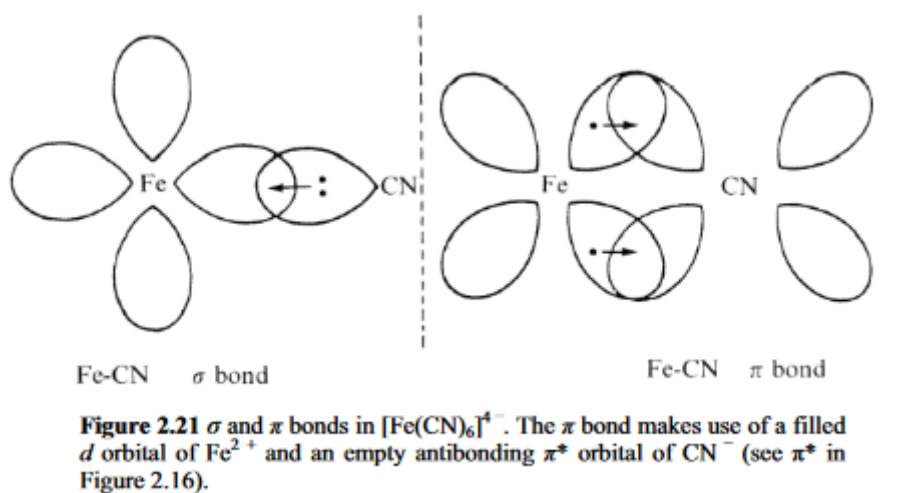


Figure 2.20 Molecular orbital diagrams for high-spin $[\text{CoF}_6]^{3-}$ and low-spin $[\text{Co}(\text{NH}_3)_6]^{3+}$.

the 4s, and the three 4p orbitals are oriented along the x,y, and z axes where the ligands are located. Therefore, orbital overlap with the ligand AO's results, and six bonding and six antibonding MO's are formed: $1s(1)$, $1p(3)$, $1d(2)$, $1d^*(2)$, $1s^*(1)$, $1p^*(3)$. The $t_{2g}(d_{xy}, d_{xz}, \text{ and } d_{yz})$ orbitals do not point at ligand orbitals and hence are not involved in bonding. Their energy is unchanged, and they are called nonbonding orbitals. When cobalt(III) and ligand electrons are placed in the complex MO's, we find that the six bonding MO's are filled; this corresponds to six metal–ligand bonds. The remaining electrons are distributed among nonbonding MO's (the t_{2g} orbitals) and $1d^*$ (antibonding) MO's. The $1d^*$ MO's arise from the interaction of metal d_{xz} and d_{yz} orbitals and ligand orbitals, but since the $1d^*$ MO's are nearer in energy to the metal d_{xz} and d_{yz} orbitals, they do not differ markedly from them. Therefore, the placement of excess electrons in t_{2g} and $1d^*$ MO's is analogous to the arrangement predicted by the crystal field model, where the same number of electrons is distributed between t_{2g} and e_g orbitals. If the difference in energy Δ_o between nonbonding t_{2g} orbitals and $1d^*$ MO is small, electrons remain unpaired; in $[\text{CoF}_6]^{3-}$ this is what happens and electrons are distributed $t_{2g}^4 1d^* 2$. The presence of two electrons in $1d^*$ orbitals effectively cancels the contribution of two electrons in bonding $1d$ orbitals and hence weakens the Co—F bonds. When Δ_o is large as in $[\text{Co}(\text{NH}_3)_6]^{3+}$, all electrons go into

t_{2g} orbitals. The reasons for the energy separation between the t_{2g} and e_g orbitals are quite different in the two theories. According to CFT the crystal field splitting arises from electrostatic repulsion of d electrons by ligands. MOT essentially attributes the splitting to covalent bonding. The greater the overlap of e_g metal orbitals with ligand orbitals, the higher in energy will be the e_g orbital. MOT can explain the influence of σ bonds on the stability of metal complexes and on the magnitude of the crystal field splitting provided by ligands. Since a quantitative treatment of this subject is quite involved, only a qualitative explanation will be presented here. In the previous discussion, it was indicated that the strength of a covalent interaction depends on the extent of overlap of AO's on the two bonded atoms. In previous examples, only σ overlap was considered. In $[\text{Fe}(\text{CN})_6]^{4-}$ and a variety of other metal complexes, both σ and π bonding occur (Figure 2.21). In the σ bond, the ligand acts as a Lewis base and shares a pair of electrons with an empty e_g orbital. In the π bond, CN^- ion acts as a Lewis acid and accepts electrons from the filled t_{2g} orbital of the metal. The presence of π bonding as well as σ bonding strengthens the metal–ligand bond and contributes to the unusual stability of the $[\text{Fe}(\text{CN})_6]^{4-}$ ion. In oxyanions, such as MnO_4^- , σ and π bonding are also both important. In this case, the ligand (oxygen) provides the electrons for the π bond. The large crystal fields that are provided by CN^- , CO , and other π -bonding ligands can be explained in this manner. The t_{2g} orbitals of a metal in an octahedral complex are oriented correctly for π bonding (Figure 2.21). As was



noted previously, the t_{2g} orbitals point between ligands and hence cannot form σ bonds. In a π bond with a ligand such as CN^- , t_{2g} electrons are partially transferred to the ligand. This process (a bonding interaction) lowers the energy of the t_{2g} orbitals. In Figure 2.8, one can see that a process that will lower the energy of t_{2g} orbitals must increase Δ_o . The preceding discussion is a simplified MO approach to bonding, but it illustrates some of the basic ideas and a little of the usefulness of the theory. MOT is very effective in handling both covalent and ionic contributions to the metal ligand bond. In conclusion, note that all three of these theories are, at best, only good approximations. All three can account qualitatively for many features of metal complexes; all three are used currently, and one or the other may be most convenient for a given application. The most versatile is MOT. Unfortunately, it is also the most complicated.