

STRUCTURE AND BONDING IN INORGANIC CHEMISTRY

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Summary

The electronic structures of metal complexes are described in terms of ligand-field theory. The $\sigma^*_{x^2-y^2}$, $\sigma^*_{z^2}$ (or $3d_{x^2-y^2}$, $3d_{z^2}$) and π_{xz} , π_{yz} , π_{xy} (or $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$) molecular orbitals in octahedral metal complexes are called *ligand-field levels*, with the $\sigma^*_{x^2-y^2}$ and $\sigma^*_{z^2}$ level at higher energy than the π_{xz} , π_{yz} , π_{xy} level. The energy separation of the $\sigma^*(d)$ and $\pi(d)$ levels is called the *octahedral ligand-field splitting*, Δ_o . The higher two orbitals commonly are denoted e_g , and the lower three orbitals are denoted t_{2g} . In most cobalt (III) complexes, Δ_o is sufficiently large to allow all six *d* electrons to fill the t_{2g} level, thereby giving the ground-state electronic structure $(t_{2g})^6$. In filling the t_{2g} and e_g energy levels, the electronic configurations d^5 , d^6 , and d^7 , as well as d^4 , can exhibit either a high-spin or a low-spin ground state, depending on the value of Δ_o in the complex. An electron in the t_{2g} level of an octahedral complex can absorb a photon in the near-infrared, visible, or ultraviolet region and make a transition to an unoccupied orbital in the more energetic e_g level. Electronic excitations of this type are called *d-d* (or ligand-field, LF) transitions. The colors of many transition metal complexes are attributable to *d-d* transitions. The ordering of ligands in terms of their ability to split the e_g and t_{2g} molecular orbitals is known as the *spectrochemical series* ($\text{CO} > \text{CN}^- > \text{NO}_2^- > \text{NH}_3 > \text{OH}_2 > \text{OH}^- > \text{F}^- > -\text{SCN}^-, \text{Cl}^- > \text{Br}^- > \text{I}^-$). The most important characteristic of the ligand-field splitting in a square planar complex is that $\sigma^*_{x^2-y^2}$ is of much higher energy than the other four orbitals; d^8 metal ions, particularly Ni^{2+} , Pd^{2+} , Pt^{2+} , and Au^{3+} , commonly exhibit square planar geometry. All d^8 square planar complexes have low-spin ground-state configurations. In a tetrahedral

complex, three $\sigma^*(d)$ orbitals are the t_2 set, and the two $\pi^*(d)$ orbitals are the e set; the difference in energy between t_2 and e is Δ_t , which is much smaller than Δ_o for a given metal ion and ligand ($\Delta_t \cong 0.45\Delta_o$). Because of the small Δ_t values, *all* tetrahedral transition-metal complexes have high-spin ground-state configurations. Absorption bands attributable to $M \rightarrow L$ or $L \rightarrow M$ charge transfer excitation are called metal-to-ligand (MLCT) or ligand-to-metal (LMCT) bands. The powerful oxidizing agent $[\text{MnO}_4]^-$ exhibits strong LMCT absorption in the visible region. MLCT bands occur at relatively low energy if the central metal atom or ion has reducing properties, and if the attached ligands have unoccupied orbitals of low enough energy to accept the electron. The reaction between a ligand and a metal ion often is classified as a *Lewis acid-base interaction*, in which the ligand (base) donates an electron pair to the metal ion (acid). Metal ions that form more stable complexes with ligands containing the donor atoms N, O, and F than with those containing P, S, and Cl are called *hard acids*; and *soft acids* are metal ions that form stronger complexes with ligands containing heavier donor atoms than with those containing N, O, and F. Most hard metal ions have high positive charges, small radii, and closed-shell (Al^{3+}) or half-filled d shell (Mn^{2+} , Fe^{3+}) configurations. Most soft metal ions have low positive charges, large radii, and nonclosed-shell configurations.

1. Introduction

The transition metals (or d -electron elements) form compounds with interesting spectroscopic and magnetic properties. *Coordination number* is defined as the number of atoms bonded directly to the central metal atom. The groups attached to the metal are called ligands. Each ligand has one or more donor atoms that bond to the metal. Coordination numbers four and six are the most common among transition-metal complexes. Almost all six-coordinate complexes have an octahedral structure. Both square planar and tetrahedral geometries are prominent for four-coordinate complexes. Many complexes of metal ions with d^8 or d^9 electronic configurations have a square planar structure: Pd^{2+} ($4d^8$), Pt^{2+} ($5d^8$), and Au^{3+} ($5d^8$) complexes are square planar. Although tetrahedral complexes are formed by many metal ions of the first transition series (Sc–Zn), the occurrence of this structure in heavier ($4d$ and $5d$ series) metal ions is restricted mainly to d^0 and d^{10} configurations.

The maximum number of σ bonds that can be constructed from s and p valence orbitals is four. Thus four is the highest coordination number commonly encountered for central atoms with $2s$ and $2p$ valence orbitals. A first-row transition metal atom has nine valence orbitals—five $3d$ orbitals, one $4s$ orbital, and three $4p$ orbitals.

If the central metal atom used all of its d , s , and p valence orbitals in σ bonding, a total of nine ligands could be attached. However, because of the large size of most ligands it is extremely difficult to achieve a coordination number of nine. Most first-row metal complexes have the coordination number six and an octahedral structure. Six of the nine valence orbitals of the central atom are used in σ bonding in an octahedral structure: $3d_{x^2-y^2}$, $3d_z^2$, $4p_x$, $4p_y$, $4p_z$, and $4s$. In localized molecular-orbital language six d^2sp^3 hybrid orbitals are used to attach the six ligands. However, the localized molecular orbital theory is inadequate for explaining the colors and magnetic properties of transition-metal complexes. The model of greatest utility emphasizes the interaction of

the d valence orbitals of the metal atoms with appropriate ligand orbitals. It is called *ligand-field theory*.

2. Ligand-field Theory for Octahedral Complexes

Consider the five $3d$ orbitals in a metal complex such as $[\text{Co}(\text{NH}_3)_6]^{3+}$. To describe the bonding we choose a coordinate system in which the X , Y , and Z axes go through the nitrogen nuclei. The $\text{Co } 3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals overlap the approximately sp^3 lone-pair orbitals of the six NH_3 groups. Appropriate linear combinations form two bonding orbitals, $\sigma_{z^2}^b$ and $\sigma_{x^2-y^2}^b$, and two antibonding orbitals, $\sigma_{z^2}^*$ and $\sigma_{x^2-y^2}^*$. The antibonding molecular orbitals $\sigma_{z^2}^*$ and $\sigma_{x^2-y^2}^*$ have much more metal than ligand character, and often are referred to simply as the “metal” $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals.

The $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$ orbitals are directed between the ligands. They are not situated properly for σ bonding in $[\text{Co}(\text{NH}_3)_6]^{3+}$. Consequently the originally degenerate five $3d$ valence orbitals, in which the electrons have equal energy in the free atom, divide into two sets in an octahedral complex. The $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are involved in the σ molecular-orbital system, whereas the $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$ orbitals are nonbonding.

The two orbital sets, $\sigma_{x^2-y^2}^*$, $\sigma_{z^2}^*$ (or $3d_{x^2-y^2}$, $3d_{z^2}$) and π_{xz} , π_{yz} , π_{xy} (or $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$) are called ligand-field levels. The $\sigma_{x^2-y^2}^*$ and $\sigma_{z^2}^*$ orbitals always have higher energy than the π_{xz} , π_{yz} , π_{xy} orbitals in an octahedral complex. The energy separation of the $\sigma^*(d)$ and $\pi(d)$ levels is called the octahedral ligand-field splitting and is abbreviated Δ_o . The higher two orbitals commonly are denoted e_g , and the lower three orbitals are denoted t_{2g} (Figure 1).

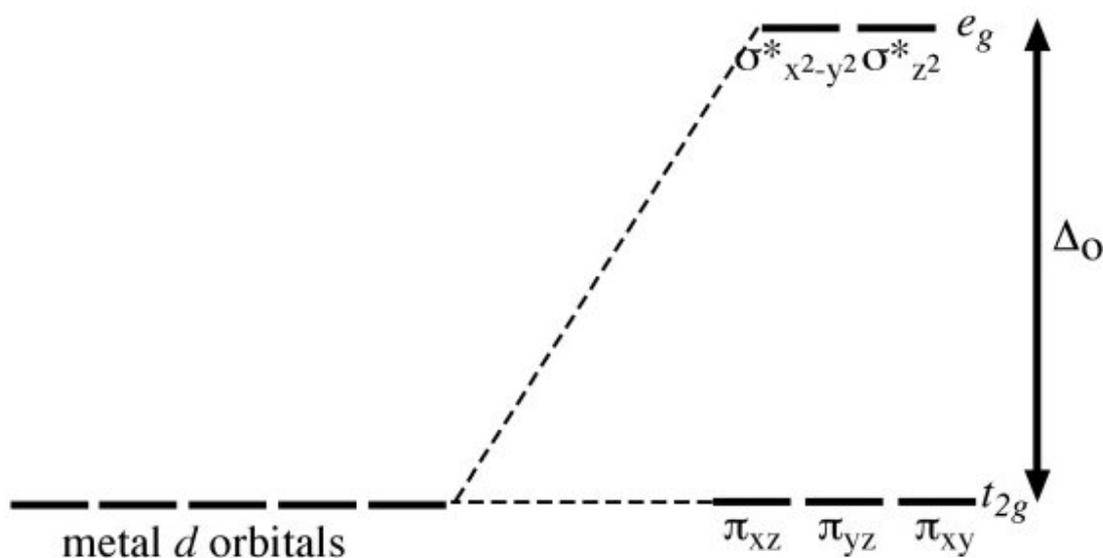


Figure 1. The higher two orbitals commonly are denoted e_g , and the lower three orbitals are denoted t_{2g}

The twelve electrons furnished by the six NH_3 ligands occupy six bonding molecular orbitals constructed from the NH_3 lone-pair orbitals and the $3d_{z^2}$, $3d_{x^2-y^2}$, $4s$, $4p_x$, $4p_y$, and $4p_z$ metal orbitals. The bonding molecular orbitals are analogous to the six d^2sp^3 bonding orbitals in the localized molecular-orbital description. The antibonding orbitals derived from the $4s$ and $4p$ metal atomic orbitals are very energetic. The orbitals of importance in formulating electronic structures of the ground and lowest excited states are the two ligand-field levels, t_{2g} and e_g . Because the valence electronic structure of Co^{3+} is $3d^6$, there are six valence electrons available to place in the t_{2g} and e_g levels. There are two possibilities, depending on the value of Δ_o . In $[\text{Co}(\text{NH}_3)_6]^{3+}$, Δ_o is sufficiently large to allow all six d electrons to fill the t_{2g} level, thereby giving the ground-state electronic structure $(t_{2g})^6$, with all electrons paired. However, if Δ_o is smaller than the required electron-pairing energy, as happens in the Co^{3+} complex $[\text{CoF}_6]^{3-}$, the d electrons occupy the t_{2g} and e_g levels to give the maximum number of unpaired spins. The ground-state structure of $[\text{CoF}_6]^{3-}$ is $(t_{2g})^4(e_g)^2$, with four unpaired electrons. Because of the difference in the number of unpaired electron spins in the two complexes, $[\text{Co}(\text{NH}_3)_6]^{3+}$ is said to be low-spin, whereas $[\text{CoF}_6]^{3-}$ is referred to as a high-spin complex.

The ground-state electronic configurations of octahedral complexes that contain central metal ions other than Co^{3+} are set out in Table 1. Listed is the number of unpaired d electrons in first-row dipositive and tripisitive transition-metal ions that commonly are observed in octahedral coordination complexes. In each case the d^n configuration and the number of unpaired d electrons for the uncomplexed metal ion are given. Metal ions with one, two, and three valence electrons have the respective ground-state configurations $(t_{2g})^1$, $(t_{2g})^2$, and $(t_{2g})^3$. There are two possible ground-state configurations for the metal d^4 configuration, depending on the value of Δ_o in the complex. If Δ_o is less than the energy required to pair two d electrons in the t_{2g} level, the fourth electron will go into the e_g level, thereby giving the high-spin configuration $(t_{2g})^3(e_g)^1$, with four unpaired electrons. Ligands that form high-spin complexes are called weak-field ligands.

Ion	Number of d electrons	Number of unpaired d electrons
Sc^{3+}	0	0
Ti^{3+}	1	1
V^{2+}	3	3
V^{3+}	2	2
Cr^{2+}	4	4
Cr^{3+}	3	3
Mn^{2+}	5	5
Fe^{2+}	6	4
Fe^{3+}	5	5
Co^{2+}	7	3
Co^{3+}	6	4
Ni^{2+}	8	2
Cu^{2+}	9	1
Zn^{2+}	10	0

Table 1. Unpaired electrons in uncomplexed metal ions.

If Δ_o is larger than the required electron-pairing energy, the fourth electron will go into the lower-energy t_{2g} level and pair with one of the three electrons already present in that level. In this situation the ground state of the complex is the low-spin configuration $(t_{2g})^4$, with only two unpaired electrons. Ligands that cause splittings large enough to allow electrons to occupy preferentially the more stable t_{2g} level to give low-spin complexes are called strong-field ligands.

In filling the t_{2g} and e_g energy levels, the electronic configurations d^5 , d^6 , and d^7 , as well as d^4 , can exhibit either a high-spin or a low-spin ground state, depending on the value of Δ_o in the complex. For a given d^n configuration the paramagnetism of a high-spin complex is larger than that of a low-spin complex. See Table 2.

Electronic configuration of the metal ion	Electronic structure of the complex	Number of unpaired electrons	Example
$3d^1$	$(t_{2g})^1$	1	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
$3d^2$	$(t_{2g})^2$	2	$[\text{V}(\text{H}_2\text{O})_6]^{3+}$
$3d^3$	$(t_{2g})^3$	3	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
$3d^4$	Low-spin; $(t_{2g})^4$	2	$[\text{Mn}(\text{CN})_6]^{3-}$
	High-spin; $(t_{2g})^3(e_g)^1$	4	$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
$3d^5$	Low-spin; $(t_{2g})^5$	1	$[\text{Fe}(\text{CN})_6]^{3-}$
	High-spin; $(t_{2g})^3(e_g)^2$	5	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
$3d^6$	Low-spin; $(t_{2g})^6$	0	$[\text{Co}(\text{NH}_3)_6]^{3+}$
	High-spin; $(t_{2g})^4(e_g)^2$	4	$[\text{CoF}_6]^{3-}$
$3d^7$	Low-spin; $(t_{2g})^6(e_g)^1$	1	$[\text{Co}(\text{NO}_2)_6]^{4-}$
	High-spin; $(t_{2g})^5(e_g)^2$	3	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
$3d^8$	$(t_{2g})^6(e_g)^2$	2	$[\text{Ni}(\text{NH}_3)_6]^{2+}$
$3d^9$	$(t_{2g})^6(e_g)^3$	1	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$

Table 2. Electronic configurations of octahedral complexes

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Biographical Sketches

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