

6.2: Electronic Structure of Complexes (Part 1)

It is necessary to learn a few concepts to understand the structure, spectrum, magnetism, and reactivity of complexes which depend on d electron configurations. In particular, the theory of electronic structure is important.

Ligand field theory

Ligand field theory is one of the most useful theories to account for the electronic structure of complexes. It originated in the application of the **crystal field theory** of ionic crystals to metal complex systems.

Six co-ordinate octahedral complexes

The five d orbitals of transition metal cations are degenerate and have equal energy.

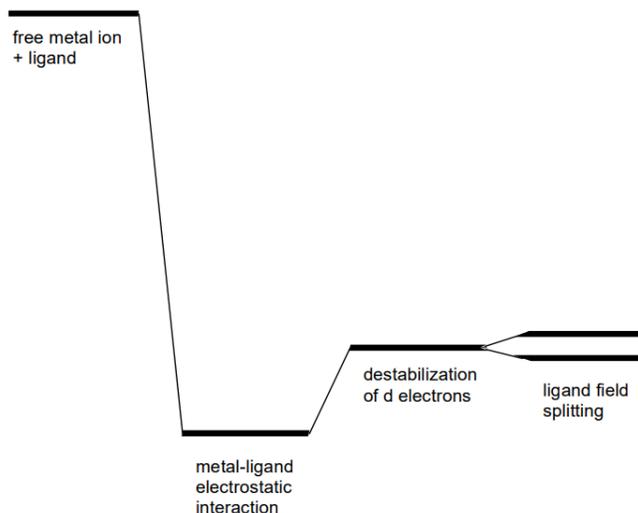


Figure 6.2.4: Change of electronic energy upon complex formation.

The spherical negative electric field around a metal cation results in the total energy level being lower than that of a free cation because the electrostatic interactions. The repulsive interaction between the electrons in the metal orbitals and the negative electric field destabilizes the system and compensates for the stabilization to some extent (Figure 6.2.4).

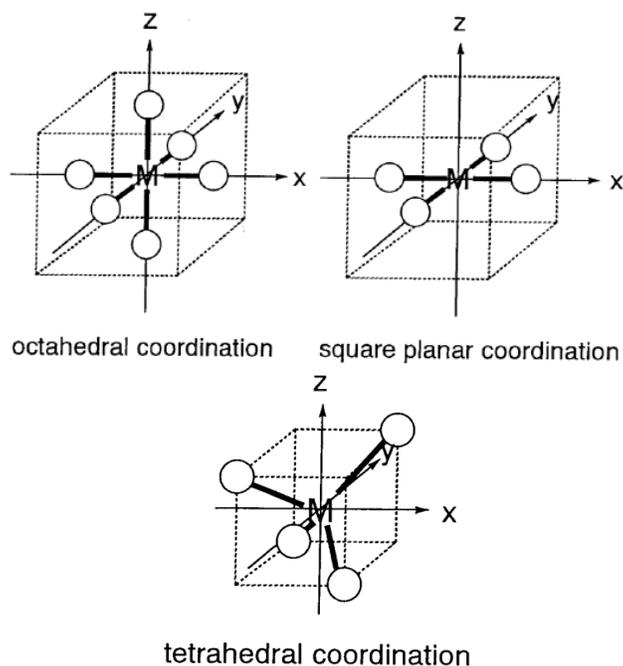


Figure 6.2.5: Ligand positions in the Cartesian coordinate with a metal ion at the origin.

Let us assume that instead of a uniform spherical negative field, the field is generated by six ligands coordinating octahedrally to a central metal. The negative field of the ligands is called the **ligand field**. Negative charge, in the case of anionic ligands, or a negative end (lone pair), in the case of neutral ligands, exert a repulsive force on the metal d orbitals which is anisotropic depending on the direction of the orbitals. The position of the metal cation is taken as the origin and Cartesian coordinates are constructed (Figure 6.2.5). Then, $d_{x^2-y^2}$ and d_{z^2} orbitals are aligned along the directions of the axes and the d_{xy} , d_{yz} , and d_{xz} orbitals are directed between the axes. If ligands are placed on the axes, the repulsive interaction is larger for the e_g orbitals ($d_{x^2-y^2}$, d_{z^2}) than for the t_{2g} orbitals (d_{xy} , d_{yz} , d_{xz}), and the e_g orbitals are destabilized and the t_{2g} orbitals are stabilized to an equal extent. In the following discussion, only the energy difference between the t_{2g} and e_g orbitals is essential and the average energy of these orbitals is taken as the zero of energy. If the energy difference between the two e_g and three t_{2g} orbitals is set to Δ_o , the energy level of the e_g orbitals is $+3/5 \Delta_o$ and that of the t_{2g} orbitals is $-2/5 \Delta_o$ (Figure 6.2.6). (Δ_o may also be expressed as $10 Dq$. In this case, the energy level of the e_g orbitals is $+6 Dq$ and that of the t_{2g} orbitals $-4 Dq$.)

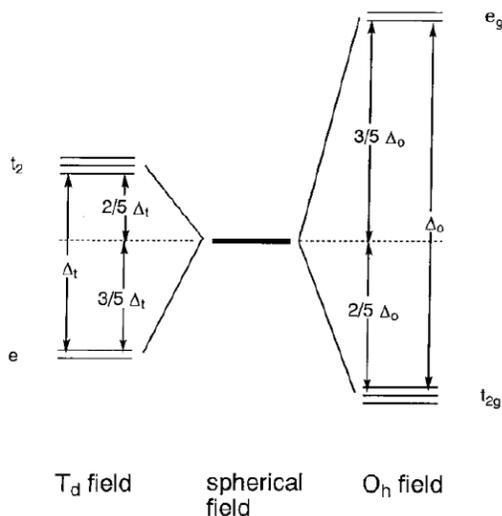


Figure 6.2.6: Ligand field splitting in tetrahedral and octahedral complexes.

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

$$LFSE = (-0.4x + 0.6y)\Delta_o$$

This value is called the **ligand field stabilization energy**. The electron configuration with 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 .

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 favoured and this is called the strong field case or the **low spin electron configuration**. If $\Delta_o < P$, $t_{2g}^3 e_g^1$ is favoured and this is called the weak field case or the **high spin electron configuration**. A similar choice is required for d^5 , d^6 , and d^7 octahedral complexes, and in the strong field case, t_{2g}^5 , t_{2g}^6 , or $t_{2g}^6 e_g^1$ configurations are favoured, whereas in the weak field case, $t_{2g}^3 e_g^2$, $t_{2g}^4 e_g^2$, or $t_{2g} e_g^2$

configurations are favoured. 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.

Square planar complexes

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 x,y 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^+ , Pd^{2+} , Pt^{2+} , and Au^{3+} complexes with a d^8 configuration tend to form square planar structures because eight electrons occupy the lower orbitals leaving the highest $d_{x^2-y^2}$ orbital empty.

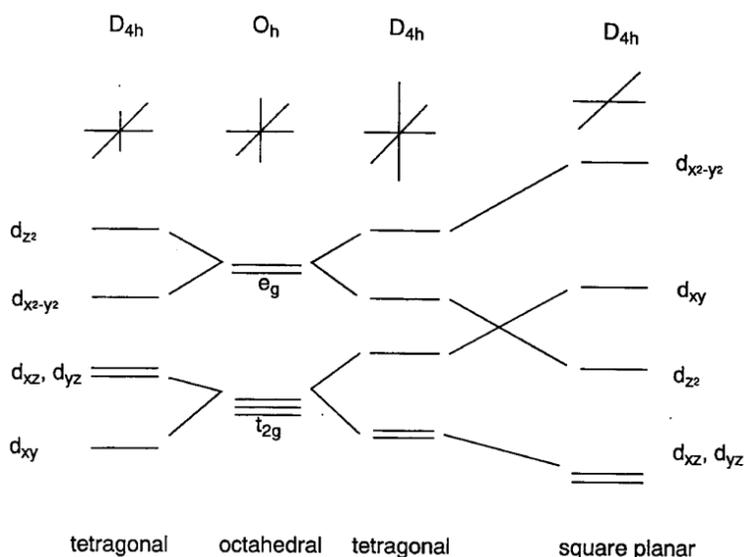


Figure 6.2.7: Change of the orbital energy from octahedral to square planar complexes.

Tetrahedral complexes

Tetrahedral complexes have four ligands on the apexes of a tetrahedron around the central metal. $[CoX_4]^{2-}$ ($X = Cl, Br, I$), $Ni(CO)_4$, etc. are all examples of 4-coordination complexes (Figure 6.2.5). When a metal is placed on the origin of the Cartesian axes, as in the octahedral complexes, e orbitals ($d_{x^2-y^2}$, d_{z^2}) are distant from ligands and t_2 orbitals (d_{xy} , d_{yz} , d_{xz}) are nearer ligands. Consequently, the electronic repulsion is larger for the t_2 orbitals, which are destabilized relative to the e orbitals. The ligand field exerted by four ligands splits the fivefold degenerate orbitals of the central metal into twofold degenerate e and threefold degenerate t_2 sets (Figure 6.2.6). The t_2 set has energy of $+2/5 \Delta_t$ and the e set $-3/5 \Delta_t$ with a ligand field splitting of Δ_t . As the number of the ligands is $4/6 = 2/3$ of that in hexacoordinate octahedral complexes, and overlap of the ligands with the orbitals is smaller, and the ligand splitting Δ_t is about a half of Δ_o . Consequently, only high-spin electron configurations are known in tetrahedral complexes. The ligand field splitting energies calculated by the above method are shown in Table 6.2.2.

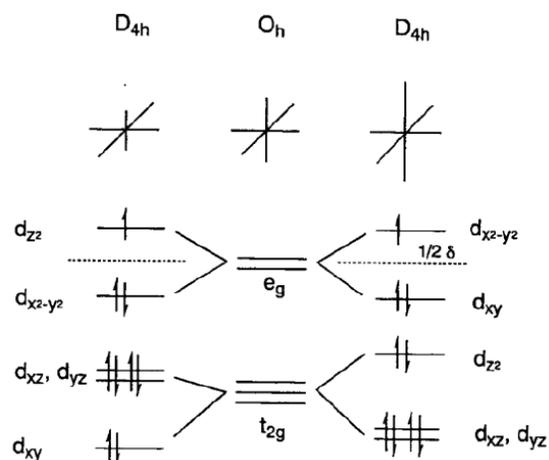
Table 6.2.2 Ligand field stabilization energy (LFSE)

		Octahedral				Tetrahedral	
		Strong field (LS)		Weak field (HS)			
d^n	Example	n	Δ_o	n	Δ_o	n	Δ_t
d^1	Ti^{3+}	1	0.4	1	0.4	1	0.6
d^2	V^{3+}	2	0.8	2	0.8	2	1.2
d^3	Cr^{3+}, V^{2+}	3	1.2	3	1.2	3	0.8

Octahedral						Tetrahedral	
d^4	$\text{Cr}^{2+}, \text{Mn}^{3+}$	2	1.6	4	0.6	4	0.4
d^5	$\text{Mn}^{2+}, \text{Fe}^{3+}$	1	2.0	5	0	5	0
d^6	$\text{Fe}^{2+}, \text{Co}^{3+}$	0	2.4	4	0.4	4	0.6
d^7	Co^{2+}	1	1.8	3	0.8	3	1.2
d^8	Ni^{2+}	2	1.2	2	1.2	2	0.8
d^9	Cu^{2+}	1	0.6	1	0.6	1	0.4
d^{10}	Cu^{1+}	0	0	0	0	0	0

Jahn-Teller Effect

When orbitals of a highly symmetrical nonlinear polyatomic molecule are degenerate, the degeneracy is resolved by distorting the molecular framework to attain lower symmetry and thus lower energy. This is the **Jahn-Teller effect** and a typical example is seen in the tetragonal distortion of an octahedral coordination structure of hexacoordinate Cu^{2+} complexes.



tetragonal octahedral tetragonal

Figure 6.2.8: Jahn-Teller splitting in a Cu^{2+} ion.

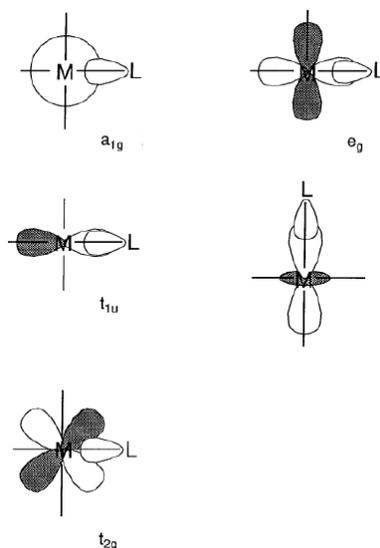


Figure 6.2.9: The relation between the metal and ligand orbitals during formation of σ bonds.

They have a d^9 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.

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