6 Chemistry of Transition Metals

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Simple substances of transition metals have properties characteristic of metals, *i.e.* they are hard, good conductors of heat and electricity, and melt and evaporate at high temperatures. Although they are used widely as simple substances and alloys, we typically encounter only iron, nickel, copper, silver, gold, platinum, or titanium in everyday life. However, molecular complexes, organometallic compounds, and solid-state compounds such as oxides, sulfides, and halides of transition metals are used in the most active research areas in modern inorganic chemistry.

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Transition elements are metallic elements that have incomplete *d* or *f* shells in the neutral or cationic states. They are called also transition metals and make up 56 of the 103 elements. These transition metals are classified into the *d*-block metals, which consist of 3*d* elements from Sc to Cu, 4*d* elements from Y to Ag, and 5*d* elements from Hf to Au, and *f*-block metals, which consist of lanthanoid elements from La to Lu and actinoid elements from Ac to Lr. Although Sc and Y belong to the *d*-block, their properties are similar to those of lanthanoids. The chemistry of *d*-block and *f*-block elements differs considerably. This chapter describes the properties and chemistry of mainly *d*-block transition metals.

6.1 Structures of metal complexes

(a) Central metals

Properties of *d*-block transition metals differ considerably between the first (3*d*) and the second series metals (4*d*), although the differences in properties between the second and the third series (5*d*) metals is not pronounced. Metallic radii of elements from scandium, Sc, to copper, Cu, (166 to 128 pm) are significantly smaller than those of yttrium, Y, to silver, Ag, (178 to 144 pm) or those of lanthanum, La, to gold, Au, (188 to 146 pm). Further, metal compounds of the first series transition metals are rarely 7 co-ordinate, whereas transition metals from the second and third series may be 7 to 9 coordinate. Cerium, Ce, (radius 182 pm) ~ lutetium, Lu, (radius 175 pm) fall between La and Hf and, because of the lanthanide contraction, metallic radii of the second and third series transition metals show little variation.

Higher oxidation states in the second and third series transition metals are considerably more stable than those in the first series transition metals. Examples include tungsten hexachloride, WCl_6, osmium tetroxide, OsO_4, and platinum hexafluoride, PtF_6. Compounds of the first series transition metals in higher oxidation states are strong oxidants and thus are readily reduced. On the other hand, whereas M(II) and M(III) compounds are common among the first series transition metals, these oxidation states are generally uncommon in compounds of second and third series metals. For example, there are relatively few Mo(III) or W(III) compounds compared with many Cr(III) ones. Aqua ions (ions with water ligands) are very common among compounds of first series metals but few are known amongst the second and third metal compounds.

Metal carbonyl cluster compounds of first series transition metals with M-M bonds in low oxidation states exist but halide or sulfide cluster compounds are rare. In general, metal-metal bonds are formed much more easily in the 4*d* and 5*d* metals than in the 3*d* ones. Magnetic moments of the first series transition metal compounds can be explained in terms of spin-only values (*cf*. Chapter 6.2 (d)) but it is difficult to account for the magnetic moments of the second and third series compounds unless complex factors such as spin-orbital interactions are taken into account.

Thus, it is necessary to acknowledge and understand the significant differences in chemical properties that exist between metals of the first and later series metal compounds, even for elements in the same group.

Properties of the *d*-block transition metals are different not only in the upper and lower positions in the periodic table but also in the left and right groups. The Group 3 to 5 metals are now often referred to as **early transition metals** and they are generally oxophilic and halophilic. Smaller numbers of *d* electrons and the hardness of these elements explain their affinity toward hard oxygen and halogens. In the absence of bridging ligands, the formation of metal-metal bonds is difficult for these elements. Organometallic compounds of these metals are known strongly to activate C-H bonds in hydrocarbons. **Late transition metals** in the groups to the right of the periodic table are soft and have a high affinity toward sulfur or selenium.

The *d*-block transition metals have *s*, *p*, and *d* orbitals and those with n electrons in the *d* orbitals are termed **ions with a d^n configuration**. For example, Ti^{3+} is a d^1 ion, and Co^{3+} a d^6 ion. The number of electrons occupying the orbitals split by the ligand field (*cf*. 6.2(a)) is denoted by a superscript on the orbital symbol. For example, an ion with 3 electrons in t_{2g} and 2 electrons in e_g is described as $t_{2g}{}^3e_g{}^1$.

(b) Ligands

Compounds of metal ions coordinated by ligands are referred to as **metal complexes**. Most ligands are neutral or anionic substances but cationic ones, such as the tropylium cation, are also known. Neutral ligands, such as ammonia, NH_3, or carbon monoxide, CO, are independently stable molecules in their free states, whereas anionic ligands, such as Cl^- or $C_5H_5^-$, are stabilized only when they are coordinated to central metals. Representative ligands are listed in Table 6.1 according to the ligating elements. Common ligands or those with complicated chemical formula are expressed in abbreviated forms.

Those ligands with a single ligating atom are called **monodentate ligands**, and those with more than one ligating atoms referred to as **polydentate ligands,** which are also called **chelate ligands**. The number of atoms bonded to a central metal is the **coordination number**.

Table 6.1 Representative ligands

Name	Abbreviation	Formula
hydrido		H^-
carbonyl		CO
cyano		CN^-
methyl	Me	CH_3^-
cyclopentadienyl	Cp	$C_5H_5^-$
carbonato		CO_3^{2-}
ammine		NH_3
pyridine	py	C_5H_5N
bipyridine	bipy	$C_{10}H_8N_2$
triphenylphosphine	PPh_3	$P(C_6H_5)_3$
aqua	aq	H_2O
acetylacetonato	acac	$CH_3C(O)CH_2C(O)CH_3^-$
thiocyanato		SCN^-
chloro		Cl^-
ethylenediaminetetraacetato	edta	$(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2^{4-}$

(c) Coordination number and structures

Molecular compounds which consist of *d*-block transition metals and ligands are referred to as complexes or **coordination compounds**. The coordination number is determined by the size of the central metal, the number of *d* electrons, or steric effects arising from the ligands. Complexes with coordination numbers between 2 and 9 are known. In particular 4 to 6 coordination are the most stable electronically and

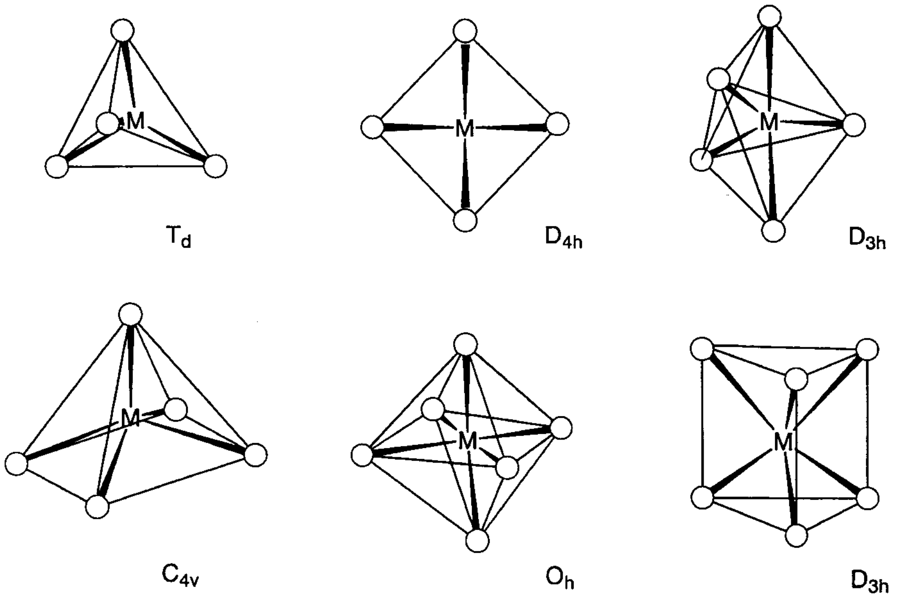


Fig. 6.1 Structure of 4 ~ 6 coordination.

geometrically and complexes with these coordination numbers are the most numerous (Fig. 6.1). Complexes with the respective coordination numbers are described below.

Two co-ordinate complexes

Many electron-rich d^{10} ions, *viz*: Cu^+, Ag^+, and Au^+, form linear complexes such as $[Cl\text{-}Ag\text{-}Cl]^-$ or $[H_3N\text{-}Au\text{-}NH_3]^-$. A zero-valent complex $[Pd(PCy_3)_2]$ with very bulky tricyclohexylphosphine ligands is also known. Generally, stable 2-coordinate complexes are known for the late transition metals.

Three co-ordinate complexes

Although $[Fe\{N(SiMe_3)_3\}_3]$ is one example, very few 3-coordinate complexes are known.

Four co-ordinate complexes

When four ligands coordinate to a metal, tetrahedral (T_d) coordination is the least congested geometry, although a number of square planar (D_{4h}) complexes are known. $[CoBr_4]^{2-}$, $Ni(CO)_4$, $[Cu(py)_4]^+$, $[AuCl_4]^-$ are all examples of tetrahedral complexes. There are a few known examples of square planar complexes with identical ligands, such as $[Ni(CN)_4]^{2-}$, or $[PdCl_4]^{2-}$. In the case of **mixed ligand complexes**, a number of square planar complexes of d^8 ions, Rh^+, Ir^+, Pd^{2+}, Pt^{2+}, and Au^{3+}, have been reported. Examples include $[RhCl(PMe_3)_3]$, $[IrCl(CO)(PMe_3)_2]$, $[NiCl_2(PEt_3)_2]$, and $[PtCl_2(NH_3)_2]$ ($Et = C_2H_5$).

Cis and trans **geometrical isomers** are possible for complexes with two different kinds of ligands, and were first noted when A. Werner synthesized 4-coordinate $[PtCl_2(NH_3)_2]$. As tetrahedral complexes do not give geometrical isomers, Werner was able to conclude that his 4-coordinate complexes were square planar. Recently *cis*-$[PtCl_2(NH_3)_2]$ (Cisplatin) has been used for the treatment of tumors and it is noteworthy that only the *cis* isomer is active.

Exercise 6.1 Write the formal name of *cis*-$[PtCl_2(NH_3)_2]$.
[Answer] *cis*-diamminedichloroplatinum.

Five co-ordinate complexes

Trigonal bipyramidal (D_{3h}) $Fe(CO)_5$ or square pyramid (C_{4v}) $VO(OH_2)_4$ are examples of 5-coordinate complexes. Previously, 5-coordinate complexes were rare but the number of new complexes with this coordination is increasing. The energy difference between the two coordination modes is not large and structural transformation readily occurs. For example, the molecular structure and infrared spectrum of $Fe(CO)_5$ are consistent with a trigonal bipyramid structure, but the ^{13}C NMR spectrum shows only one signal at the possible lowest temperature, which indicates that the axial and equatorial carbonyl ligands are fluxional in the NMR time scale (10^{-1}~10^{-9} s). Structural transformation takes place via a square pyramid structure and the mechanism is well known as **Berry's pseudorotation**.

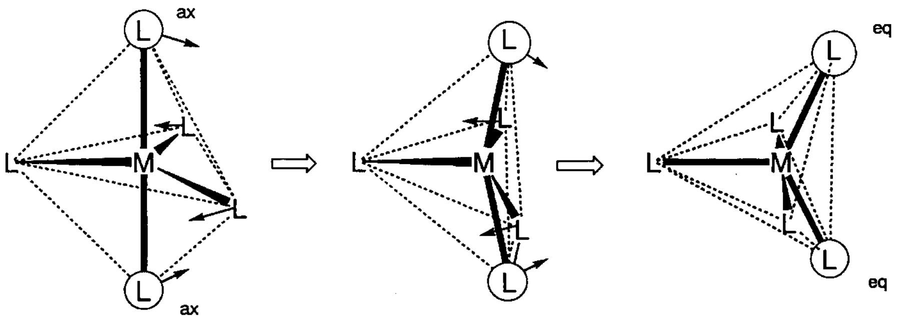
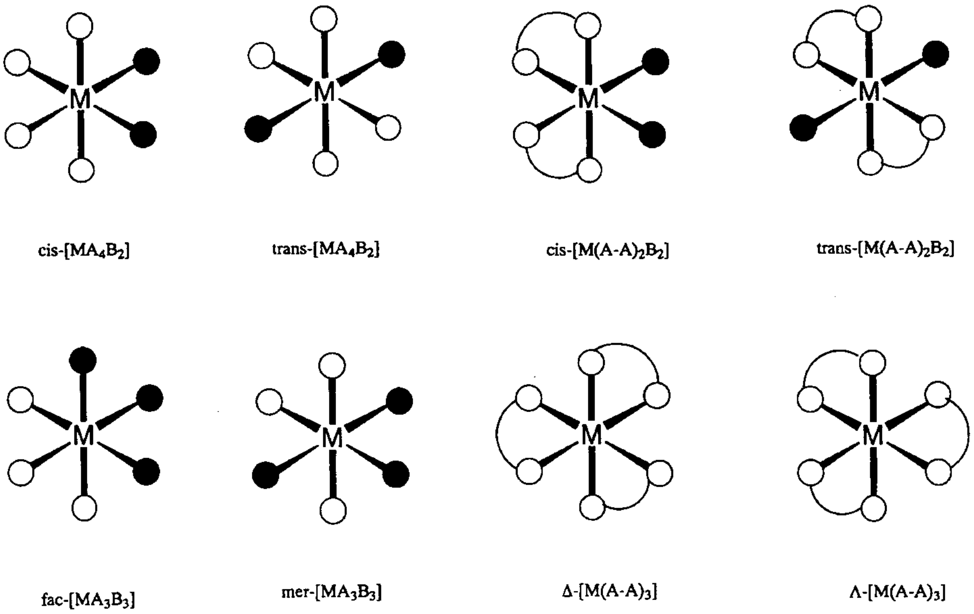


Fig. 6.2 Berry's pseudorotation.

Six co-ordinate complexes

When six ligands coordinate to a central metal, octahedral (O_h) coordination is the most stable geometry and the majority of such complexes assume this structure. In particular, there are a number of Cr^{3+} and Co^{3+} complexes which are inert to ligand exchange reactions, represented by $[Cr(NH_3)_6]^{3+}$ or $[Co(NH_3)_6]^{3+}$. They have been particularly important in the history of the development of coordination chemistry. $[Mo(CO)_6]$, $[RhCl_6]^{3-}$, *etc*. are also octahedral complexes. In the case of mixed ligands, *cis*- and *trans*-$[MA_4B_2]$ and *mer*- and *fac*-$[MA_3B_3]$ geometrical isomers, and for chelate ligands, Δ-$[M(A\text{-}A)_3]$ and Λ-$[M(A\text{-}A)_3]$ **optical isomers** (Fig. 6.3) are possible. The octahedral structure shows tetragonal (D_{4h}), rhombic (D_{2h}), or trigonal (D_{3h}) distortions caused by electronic or steric effects. The tetragonal distortion of $[Cu(NH_3)_6]^{2+}$ by an electronic factor is a typical example of the Jahn-Teller effect (refer to 6.2(a)).



cis-$[MA_4B_2]$ trans-$[MA_4B_2]$ cis-$[M(A\text{-}A)_2B_2]$ trans-$[M(A\text{-}A)_2B_2]$

fac-$[MA_3B_3]$ mer-$[MA_3B_3]$ Δ-$[M(A\text{-}A)_3]$ Λ-$[M(A\text{-}A)_3]$

Fig. 6.3 Geometrical isomers of 6-coordination.

Six ligating atoms can assume trigonal prism coordination. Although this coordination is seen in $[Zr(CH_3)_6]^{2-}$ or $[Re\{S_2C_2(CF_3)_2\}_3]$, few metal complexes with this coordination structure are known because octahedral coordination is sterically less strained. This notwithstanding, it has long been known that the bonding mode of sulfur atoms around a metal is trigonal prism in solid-state MoS_2 and WS_2.

Exercise 6.2 Write the chemical formula of potassium diamminetetra(isothiocyanato)chromate(III).

[Answer] $K[Cr(NCS)_4(NH_3)_2]$.

Higher co-ordinate complexes

Metal ions of the second and third transition metal series can sometimes bond with more than seven ligating atoms and examples are $[Mo(CN)_8]^{3-}$ or $[ReH_9]^{2-}$. In these cases, smaller ligands are favorable to reduce steric congestion.

6.2 Electronic structure of complexes

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.

(a) 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.

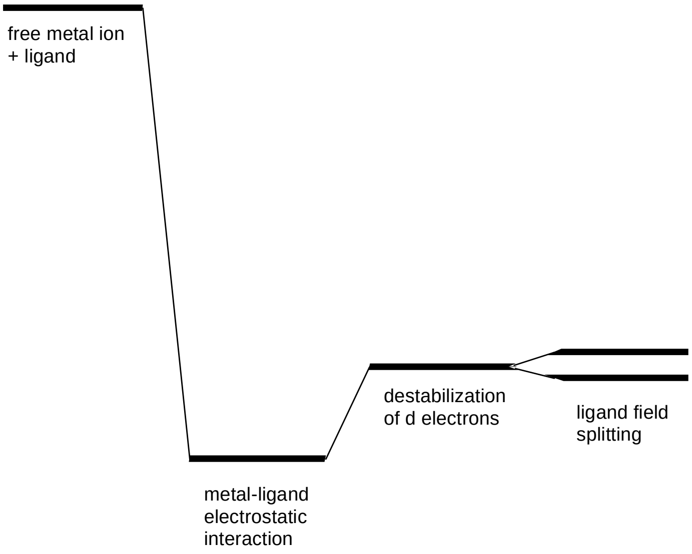
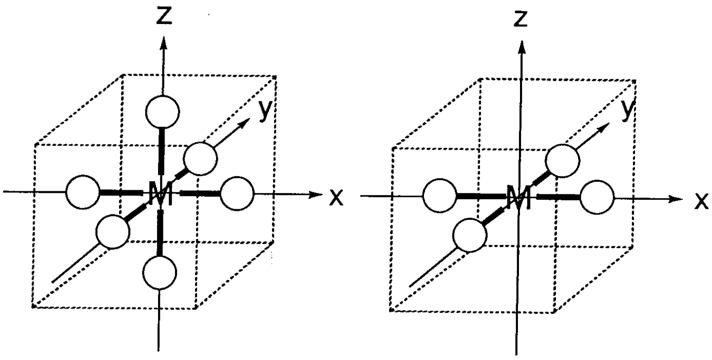
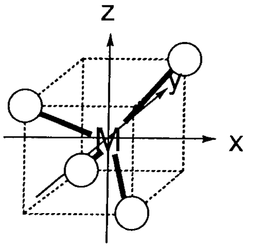


Fig. 6.4 Change of electronic energy upon complex formation.

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 (Fig. 6.4).



octahedral coordination   square planar coordination



tetrahedral coordination

Fig. 6.5 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 (Fig. 6.5). Then, d_{x2-y2} and d_{z2} 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_{x2-y2}, d_{z2}) 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 $-2/5\Delta_o$ (Fig. 6.6). (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.)

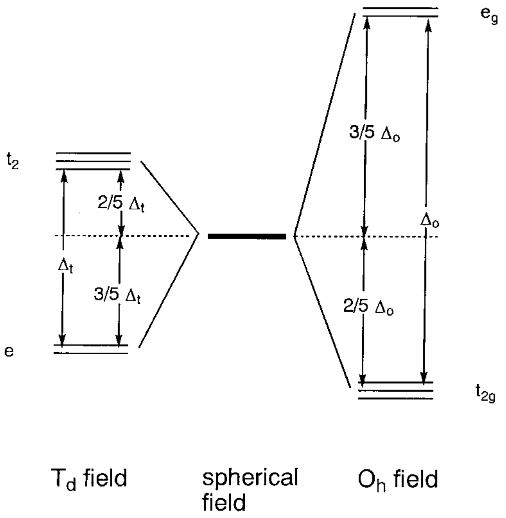


Fig. 6.6 Ligand field splitting in tetrahedral and octahedral complexes.

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

$$\text{LFSE} = (-0.4x + 0.6y)\ \Delta o$$

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 $\Delta o < P$, $t_{2g}{}^3e_g{}^1$ 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 $t_{2g}{}^6e_g{}^1$ configurations are favoured, whereas in the weak field case, $t_{2g}{}^3e_g{}^2$, $t_{2g}{}^4e_g{}^2$, or $t_{2g}{}^5e_g{}^2$ configurations are favoured. The ligand field splitting parameter Δo 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_{z2}, 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_{x2-y2} 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}, $d_{yz} < d_{z2} < d_{xy} << d_{x2-y2}$ (Fig. 6.7). 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_{x2-y2} orbital empty.

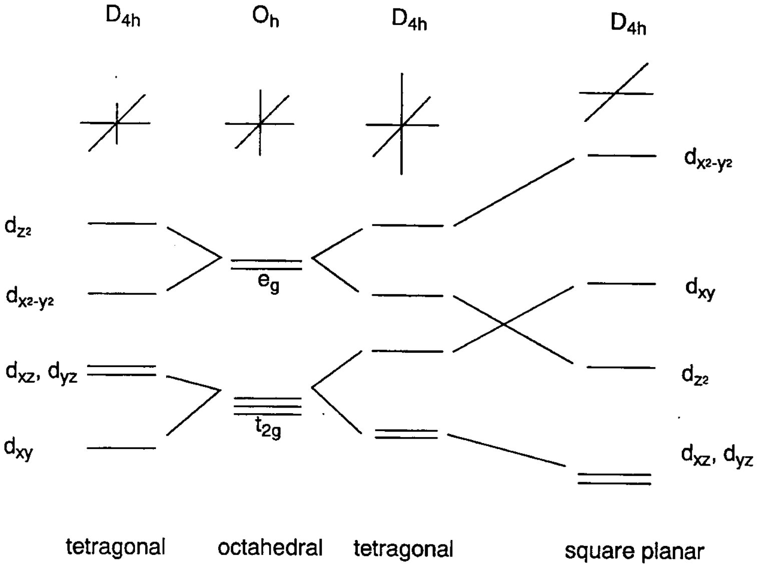


Fig. 6.7 Change of the orbital energy from octahedral to square planar complexes.

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 (Fig. 6.5). When a metal is placed on the origin of the Cartesian axes, as in the octahedral complexes, *e* orbitals (d_{x2-y2}, d_{z2}) 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 (Fig. 6.6). 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 Δt is about a half of Δo. 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.

Table 6.2 Ligand field stabilization energy (LFSE)

		Octahedral				Tetrahedral	
		Strong field (LS)		Weak field(HS)			
d^n	Example	n	Δo	n	Δo	n	Δt
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
d^4	Cr^{2},Mn^{3+}	2	1.6	4	0.6	4	0.4
d^5	Mn^{2+},Fe^{3+}	1	2.0	5	0	5	0
d^6	Fe^{2+},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.

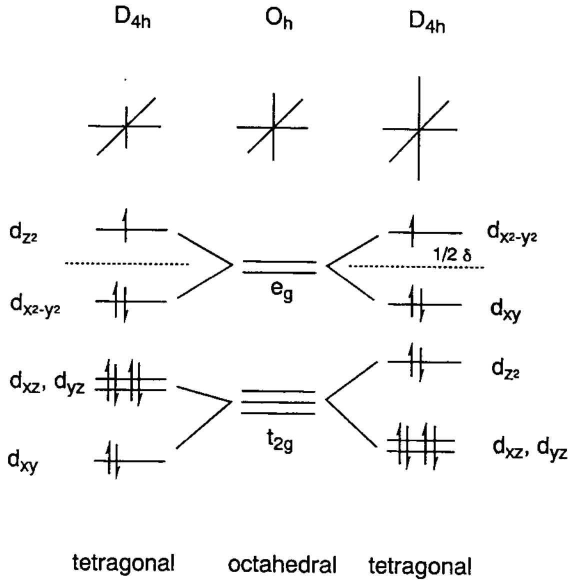


Fig. 6.8 Jahn-Teller splitting in a Cu^{2+} ion.

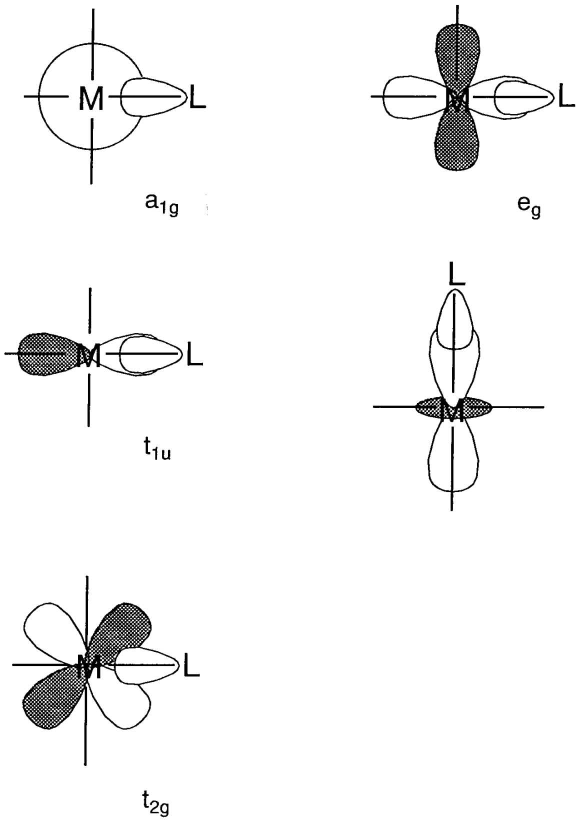


Fig. 6.9 The relation between the metal and ligand orbitals during formation of σ bonds.

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.

Molecular orbital theory of transition metal complexes

The characteristics of transition metal-ligand bonds become clear by an analysis of the molecular orbitals of a 3*d* metal coordinated by six identical ligands in octahedral complexes [ML$_6$]. As the result of the interaction between the metal *d* and ligand orbitals, bonding, non-bonding and anti-bonding complex molecular orbitals are formed.

Generally, the energy levels of the ligand orbitals are lower than those of the metal orbitals, bonding orbitals have more ligand character and non-bonding and anti-bonding orbitals have more metal character. The processes of formation of the σ and π molecular orbitals are described step by step below.

σ bond

Firstly, consider the M-L σ bond among interactions of the metal *s*, *p*, *d* and ligand orbitals by assuming the position of a metal at the origin of the Cartesian coordinate system and locating ligands on the coordinate axes. As the σ bond is a nodeless bond along the bonding axes, the metal *s* orbital (a_{1g}, non-degenerate), p_x, p_y, p_z orbitals (t_{1u}, triply-degenerate), and d_{x2-y2}, d_{z2} orbitals (e_g, doubly-degenerate) fit symmetry (+, - signs) and orbital shapes with the ligands' σ orbitals (Fig. 6.9).

When the ligand orbitals are σ_1 and σ_2 along the x-axis, σ_3 and σ_4 along the y-axis, and σ_5 and σ_6 along the z-axis in Fig. 6.5, six ligand atomic orbitals are grouped by making linear combinations according to the symmetry of the metal orbitals. Then the orbital to fit with the metal a_{1g} orbital is a_{1g} ($\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6$), the one to fit with the metal t_{1u} orbitals is t_{1u} ($\sigma_1-\sigma_2$, $\sigma_3-\sigma_4$, $\sigma_5-\sigma_6$) and the one to fit with the metal e_g orbitals is e_g ($\sigma_1+\sigma_2-\sigma_3-\sigma_4$, $2\sigma_5+2\sigma_6-\sigma_1-\sigma_2-\sigma_3-\sigma_4$). There is a bonding interaction between the metal e_g orbitals and the ligand group orbitals and bonding and anti-bonding molecular orbitals are formed. The relation is shown in Fig. 6.10.

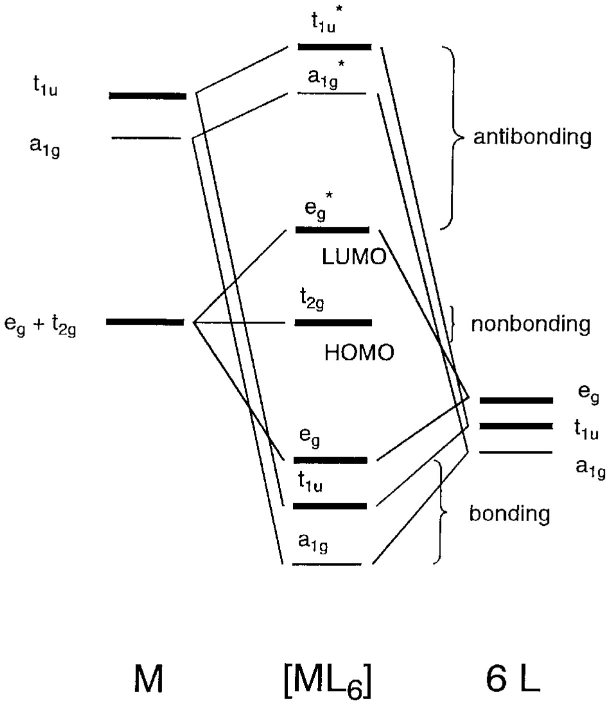


Fig. 6.10 Bonding and anti-bonding M(metal)-L(ligand) molecular orbitals.

The levels of the molecular orbitals from the lowest energy are bonding ($a_{1g}<t_{1u}<e_g$) < non-bonding (t_{2g}) < anti-bonding ($e_g^*<a_{1g}^*<t_{1u}^*$). For example, in a complex like $[Co(NH_3)_6]^{3+}$, 18 valence electrons, 6 from cobalt and 12 from ammonia, occupy 9

orbitals from the bottom up, and t_{2g} is the HOMO and e_g^* the LUMO. The energy difference between the two levels corresponds to the ligand field splitting. Namely, the e_g set ($d_{x2-y2,}$ d_{z2}) and the ligands on the corner of the octahedron form the bonding σ orbitals but the t_{2g} set (d_{xy}, d_{yz}, d_{xz}) remain non-bonding because the orbitals are not directed to the ligand σ orbitals.

π bond

When the ligand atomic orbitals have π symmetry (i.e. with nodes) through the bond axis, the e_g orbitals (d_{x2-y2}) are non-bonding and the t_{2g} orbitals (d_{xy}, d_{yz}, d_{xz}) have bonding interactions with them (Fig. 6.11). In halide ions, X^-, or aqua ligands, H_2O, the π symmetrical *p* orbitals have lower energy than the metal t_{2g} orbitals and a bonding molecular orbital, which is lower than the t_{2g} orbital, and an anti-bonding molecular

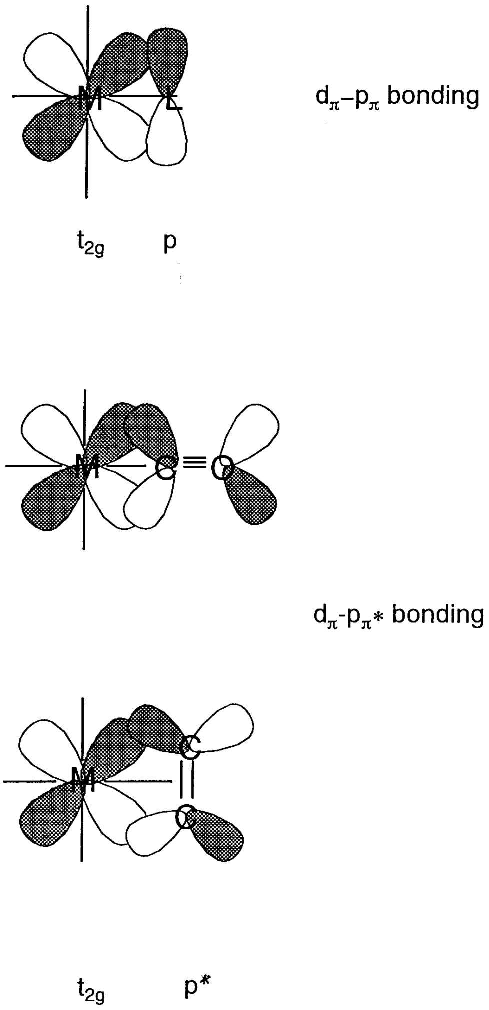


Fig. 6.11 The relation between the metal and ligand orbitals in formation of a π bond.

orbital, which is higher than the t_{2g} orbitals, form. Consequently, the energy difference Δ_o between e_g and the anti-bonding orbitals becomes smaller. On the other hand, for the ligands having anti-bonding π orbitals within the molecule, such as carbon monoxide or ethylene, the π^* orbitals match the shape and symmetry of the t_{2g} orbitals and the molecular orbitals shown in Fig 6.12 (b) form. As a result, the energy level of the bonding orbitals decreases and Δ_o becomes larger.

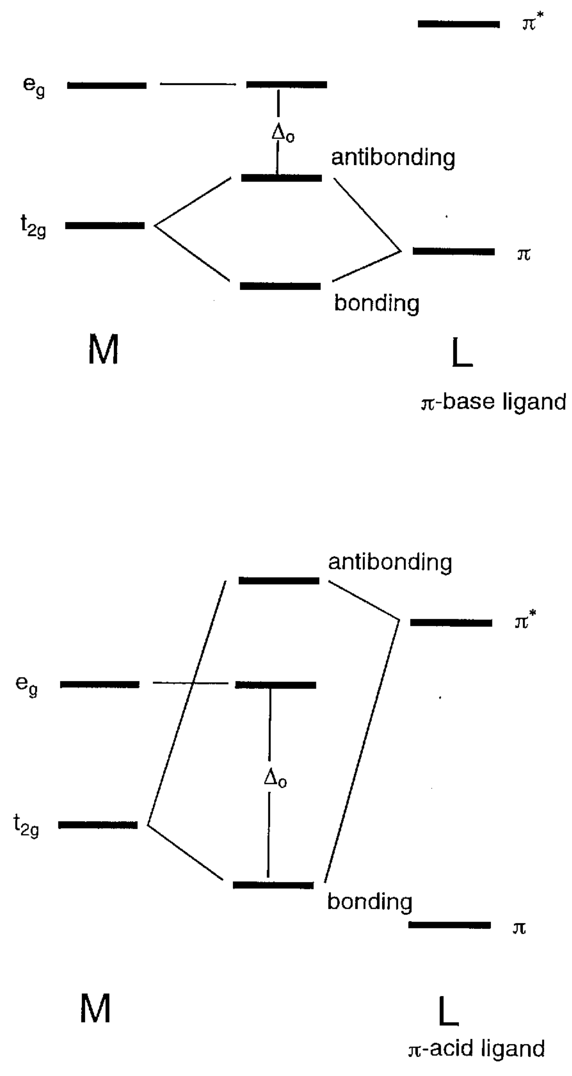


Fig. 6.12 The energy change upon formation of M-L_π bonds.

Using these simple molecular orbital considerations, the effects of σ and π orbital interactions between the metal and ligands upon the molecular orbitals are qualitatively understandable.

(c) Spectra

Many transition metal complexes have characteristic colors. This means that there is absorption in the visible part of the spectrum resulting from an electron being excited by visible light from a level occupied by an electron in a molecular orbital of the complex to an empty level. If the energy difference between the orbitals capable of transition is set to ΔE, the absorption frequency ν is given by $\Delta E = h\,\nu$. Electronic transitions by optical pumping are broadly classified into two groups. When both of the molecular orbitals between which a transition is possible have mainly metal *d* character, the transition is called a ***d-d* transition** or **ligand-field transition**, and absorption wavelength depends strongly on the ligand-field splitting. When one of the two orbitals has mainly metal character and the other has a large degree of ligand character, the transition is called a **charge-transfer transition**. Charge transfer transitions are classified into metal (M) to ligand (L) charge-transfers (MLCT) and ligand to metal charge-transfers (LMCT).

Since the analysis of the spectra of octahedral complexes is comparatively easy, they have been studied in detail for many years. When a complex has only one *d* electron, the analysis is simple. For example, Ti in $[\mathrm{Ti(OH_2)_6}]^{3+}$ is a d^1 ion, and an electron occupies the t_{2g} orbital produced by the octahedral ligand field splitting. The complex is purple as the result of having an absorption at 492 nm (20300 $\mathrm{cm^{-1}}$) (Fig. 6.13) corresponding to the optical pumping of a *d* electron to the e_g orbital. However, in a complex with more than one *d* electrons, there are repellent interactions between the electrons, and the *d-d* transition spectrum has more than one absorptions. For example, a d^3 complex $[\mathrm{Cr(NH_3)_6}]^{3+}$ shows two *d-d* absorptions in the 400 nm (25000 $\mathrm{cm^{-1}}$) region, suggesting that the complex has two groups of molecular orbitals between which an electronic transition is possible with a high degree of transition probability. This means that, when three electrons in the t_{2g} orbital are excited to the e_g orbital, there are two energy differences due to repellent interactions between the electrons.

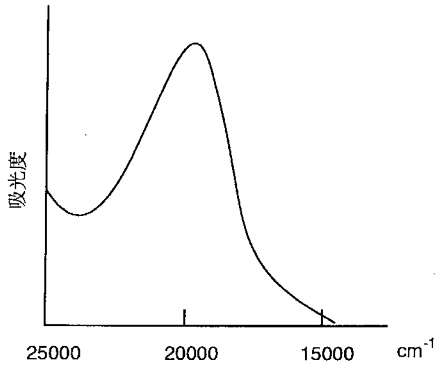


Fig. 6.13 A visible absorption spectrum of $[Ti(OH_2)_6]^{3+}$.

Tanabe-Sugano diagrams are constructed from calculations based on ligand field theory and have been widely used in the analysis of absorption spectra of d^1 to d^9 ions. The analysis becomes increasingly difficult for ions with many electrons. In any case, the existence of a *d-d* spectrum requires that the energy difference of an occupied orbital and an empty orbital is equivalent to the energy of the UV-visible spectrum, the transition is allowed by the selection rule, and the transition probability is high enough. Generally, a charge-transfer absorption is stronger than a ligand field absorption. An LMCT emerges when ligands have a non-bonding electron pair of comparatively high energy or the metal has empty low energy orbitals. On the other hand, an MLCT tends to appear when the ligands have low energy π^* orbitals, and bipyridine complexes are good examples of this. Since the lifetime of the excited state of a ruthenium complex $[Ru(bipy)_3]^{2+}$ is extraordinarily long, many studies have been performed on its photoredox reactions.

Spectrochemical series

The magnitude of the ligand field splitting parameter Δo is determined mainly by the identity of the ligands. An empirical rule called the **spectrochemical series** was proposed by a Japanese scientist Ryutaro Tsuchida. The rule was constructed from empirical data collected when spectra of complexes that have the same central metal, oxidation state, coordination number, *etc.* were measured. It is noteworthy that ligands with π acceptor properties are in a higher position in the series.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < OH^- < H_2O < NH_3 < NO_2 < PPh_3 < CN^- < CO$

Although Δ_0 does become larger in this order, it is also dependent on the identity of the central metal and its oxidation state. Namely, Δo is larger for 4*d* and 5*d* metals than for 3*d* metals and becomes larger as the oxidation number increases. The magnitude of Δ_0 is closely related to its absorption position in the electromagnetic spectrum, and is a key factor in determining the position of a ligand in the spectrochemical series. A π donor ligand (halogen, aqua, *etc*.) makes the absorption wavelength longer, and a π acceptor ligand (carbonyl, olefin, *etc*.) shorter by contribution from the π bond.

(d) Magnetism

Magnetization, M, (magnetic dipole moment per unit volume) of a sample in a magnetic field, H, is proportional to magnitude of H, and the proportionality constant, χ, depends on the sample.

$$M = \chi H$$

χ is the **volume susceptibility** and the product of χ and the molar volume V_m of a sample is the **molar susceptibility** χ_m. Namely,

$$\chi_m = \chi V_m$$

All substances have diamagnetism, and in addition to this, substances with unpaired electrons exhibit paramagnetism, the magnitude of which is about 100 times larger than that of diamagnetism. **Curie's law** shows that paramagnetism is inversely proportional to temperature.

$$\chi_m = \mathrm{A} + \frac{\mathrm{C}}{T}$$

where T is the absolute temperature and A and C are constants . In the Gouy or Faraday methods, magnetic moments are calculated from the change of weight of a sample suspended between magnets when a magnetic field is applied. In addition to these methods, the highly sensitive SQUID (superconducting quantum interference device) has been used recently to carry out such measurements.

Paramagnetism is induced by the permanent magnetic moment of an unpaired electron in a molecule and the molar susceptibility is proportional to the electron spin angular momentum. Paramagnetic complexes of *d*-block transition metals have unpaired electrons of spin quantum number 1/2, and a half of the number of unpaired electrons is the total spin quantum number S.

Therefore, the magnetic moment based only on spins
can be derived theoretically.

$$\mu = 2\sqrt{S(S+1)}\mu_B = \sqrt{n(n+2)}\mu_B$$

Here $\mu_B = 9.274 \times 10^{-24}$ JT^{-1} is a unit called the Bohr magneton.

Many 3*d* metal complexes show good agreement between the magnetic moments of paramagnetic complexes measured by a magnetic balance with the values calculated by the above formula. The relationship between the number of unpaired electrons and magnetic susceptibility of a complex is shown in Table 6.3. Because of this agreement with theory, it is possible to determine the number of unpaired electrons from experimental values of magnetic measurements. For example, it can be assumed that a Fe^{3+} d^5 complex with a magnetic moment of about 1.7 μ_B is a low-spin complex with an unpaired spin but a Fe^{3+} d^5 complex with a moment of about 5.9 μ_B is a high-spin complex with 5 unpaired electrons.

Table 6.3 Unpaired electrons and magnetic moments

Metal ion	Unpaired electron n	Spin-only magnetic moment (μ/μ_B) Calculated	Measured
Ti^{3+}	1	1.73	1.7~1.8
V^{3+}	2	2.83	2.7~2.9
Cr^{3+}	3	3.87	3.8
Mn^{3+}	4	4.90	4.8~4.9
Fe^{3+}	5	5.92	5.9

However, the measured magnetic moment no longer agrees with the calculated spin-only value when the orbital angular momentum contribution to the magnetic moment becomes large.. Especially in 5*d* metal complexes, this discrepancy between the measured and calculated values increases.

Exercise 6.3 Calculate the spin-only magnetic moments of high spin and low spin Fe^{3+} complexes.

"Answer" Since they are d^6 complexes, a high spin complex has four unpaired electrons with the magnetic moment is $4.90\mu_B$ and a low spin complex has no unpaired electron and is diamagnetic.

Some paramagnetic solid materials become **ferromagnetic** at low temperatures by forming **magnetic domains** in which thousands of electron spins are aligned parallel to each other. The temperature at which the paramagnetic-ferromagnetic phase transition occurs is called the **Curie temperature**. When spins are aligned antiparallel to each other, the material changes to an **antiferromagnetic substance**, and this transition temperature is called the **Néel temperature**. The material becomes ferrimagnetic when the spins are incompletely canceled. Recently, attempts have been made to synthesize polynuclear multi-spin complexes with special ligands that make paramagnetic metal ions align to induce ferromagnetic interactions between the spins. This effect is impossible in mononuclear complexes.

6.3 Organometallic Chemistry of d Block Metals

The organometallic chemistry of transition metals is comparatively new. Although an ethylene complex of platinum called **Zeise's salt**, $K[PtCl_3(C_2H_4)]$, tetracarbonylnickel, $Ni(CO)_4$, and pentacarbonyliron, $Fe(CO)_5$, which today are classified as organometallic compounds, were prepared in the 19th century, their bonding and structures were unknown. The research of W. Hieber and others on metal carbonyl compounds was important in the 1930s, but the results of these studies were limited because of the underdeveloped techniques of structural analyses available at the time.

The discovery of ferrocene, $Fe(C_5H_5)_2$, in 1951 was epoch-making for the chemistry of this field. The very unique bonding mode of this complex became clear by means of single crystal X-ray structural analysis, NMR spectra, infrared spectra, *etc*., and served as a starting point for subsequent developments in the field. It was a major discovery that ferrocene exhibited very high thermal stability in spite of the general view that the transition metal-carbon bonds were very unstable. It was also clearly demonstrated that the compound had a sandwich structure in which the five carbon atoms of the cyclopentadienyl groups bonded simultaneously to the central metal iron. While the various coordination modes of hydrocarbon ligands were determined one after another, the industrial importance of organometallic compounds of transition metals increased with the discoveries of olefin polymerization catalysts (Ziegler catalyst), homogeneous hydrogenation catalysts (Wilkinson catalyst), and development of catalysts for asymmetric synthesis, *etc*. The Nobel prize awarded to K. Ziegler, G. Natta (1963), E. O. Fischer, and G. Wilkinson (1973) was in recognition of this importance.

According to the definition of an organometallic compound, at least one direct bond between a metal and a carbon atom should exist, but CN complexes *etc*. with no organometallic character are usually excluded from organometallic compounds. Metal carbonyl compounds are organometallic in various aspects of their bonding, structure and reactions, and they are a good model system for understanding of the essence of transition metal organometallic chemistry.

(a) Metal carbonyl compounds

Binary metal carbonyl compounds that consist only of a metal and CO ligands are usually prepared by the direct reaction of the powder of a highly reactive metal and carbon monoxide, or by the reduction of a metal salt to zero valance followed by reaction with high-pressure carbon monoxide. However, tetracarbonylnickel, first discovered at the end of the 19th century, forms by the reaction of nickel metal and carbon monoxide under atmospheric pressure and at room temperature. The preparation of other metal carbonyl compounds, on the other hand, requires high temperatures and high pressures.

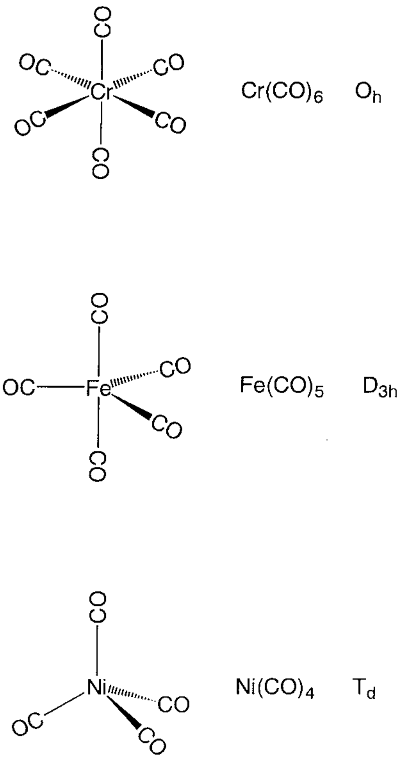


Fig. 6.14 Structures of metal carbonyl compounds.

Mononuclear metal carbonyl compounds take highly symmetric polyhedral coordination structures. Hexa-coordinate chromium, molybdenum, and tungsten hexacarbonyl, $M(CO)_6$, assume a regular octahedral, penta-coordinate pentacarbonyliron,

$Fe(CO)_5$, a triangular bipyramid, and tetracarbonylnickel, $Ni(CO)_4$, a regular tetrahedron coordination structure (Fig. 6.14). The carbon atoms of carbonyl ligands coordinate to the metal, and the CO moieties are oriented along the direction of the metal-carbon axis. Binuclear metal carbonyl $Mn_2(CO)_{10}$ has an Mn-Mn bond joining two square pyramidal $Mn(CO)_5$ parts. In $Fe_2(CO)_9$, two $Fe(CO)_3$ sub-units are bridged by three CO ligands, and in $Co_2(CO)_8$, two $Co(CO)_3$ sub-units are connected by both three CO bridges and a Co-Co bond.

There are a number of cluster metal carbonyl compounds with metal-metal bonds joining three or more metals, and terminal CO, μ-CO (a bridge between two metals), and μ_3-CO (a bridge capping three metals) are coordinated to the metal frames (refer to Section 6.3 (f)). Many cluster carbonyls are formed by a pyrolysis reaction of mononuclear or binuclear carbonyl compounds. Typical metal carbonyl compounds and their properties are shown in Table 6.4.

Table 6.4 Stable metal carbonyl compounds

	5	6	7	8	9	10
4	$V(CO)_6$ Black solid d.70	$Cr(CO)_6$ White solid d.130	$Mn_2(CO)_{10}$ Yellow solid mp 154	$Fe(CO)_5$ Yellow liquid bp 103	$Co_2(CO)_8$ Red solid mp 51	$Ni(CO)_4$ Colorless liquid bp 42.1
5		$Mo(CO)_6$ White solid sublime	$Tc_2(CO)_{10}$ White solid mp 160	$Ru_3(CO)_{12}$ Orange solid d.150	$Rh_6(CO)_{16}$ Black solid d.220	
6		$W(CO)_6$ White solid sublime	$Re_2(CO)_{10}$ White solid mp 177	$Os_3(CO)_{12}$ Orange solid mp 224	$Ir_4(CO)_{12}$ Yellow solid d.220	

Back donation

A metal carbonyl compound consists of carbon monoxide coordinated to a zero valent metal. For a long time, it had been unclear why such bonding was possible, let alone stable at all. The belief that normal coordination bonds were formed by the donation of electrons from highly basic ligands to a metal formed the basis of the coordination theory of A. Werner. Because the basicity of carbon monoxide is very low, and transition metal-carbon bonds are generally not very stable, a suitable explanation for the stability of metal carbonyl compounds was sought. If the shape and symmetry of the metal *d* orbital and of the CO π (antibonding) orbital for the carbon-oxygen bond are suitable for overlap, a bonding interaction between the metal and carbon is expected. The bonding scheme shown in Fig. 6.15 was proposed from this point of view. The mechanism by which electrons are donated to the vacant carbon monoxide π* orbital from the filled metal *d* orbital is called **back donation**. Since accumulation of superfluous electrons on a low oxidation state metal atom is prevented, back-donation leads to the stabilization of the M-C bond.

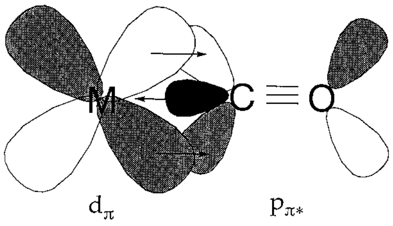


Fig 6.15 Back donation in metal carbonyls.

A rise in the order of the metal - carbon bond is reflected in the increase of the M-C, and decrease of the C-O, stretching frequencies in vibrational spectra. Infrared spectra are useful because carbonyl frequencies are easily detectable. The lowering of the oxidation state of a metal by the flow of negative charge from its coordinated ligands is reflected in the reduction of the C-O stretching frequencies.

(b) Hydrocarbon complexes

An organometallic compound is one which has metal-carbon bonds, and between one and eight carbon atoms in a hydrocarbon ligand bond to a metal. **Hapticity** describes the number of atoms in a ligand that have direct coordinative interaction with the metal and the number is added to η. An example is η^5 (pentahapto)-cyclopentadienyl (Table 6.5).

A ligand that donates an odd number of electrons to a metal is formally a radical and it is stabilized by bonding to the metal. A ligand that donates an even number of electrons to a metal is generally a neutral molecule and it is stable even if it is not bonded to the metal. Carbene or carbyne ligands are exceptions to this rule. The chemical formula of an organometallic compound is expressed in many cases without using the square brackets [ ] usual for such a complex, and we shall follow this convention in this book.

Table 6.5 Hapticity and number of donating electrons of hydrocarbon ligands

Name	Hapticity	Number of electrons	Example
Alkyl	η^1	1	$W(CH_3)_6$
Alkylidene	η^1	2	$Cr(CO)_5\{C(OCH_3)C_6H_5\}$
Alkene	η^2	2	$K[PtCl_3(C_2H_4)]$
π-allyl	η^3	3	$Ni(\eta^3\text{-}C_3H_5)_2$
Diene	η^4	4	$Fe(CO)_3(\eta^4\text{-}C_4H_6)$
Cyclopentadienyl	η^5	5	$Fe(\eta^5\text{-}C_5H_5)_2$
Arene	η^6	6	$Cr(\eta^6\text{-}C_6H_6)_2$
Tropylium	η^7	7	$V(CO)_3(\eta^7\text{-}C_7H_7)$
Cyclooctatetraene	η^8	8	$U(\eta^8\text{-}C_8H_8)_2$

Exercise 6.4 Describe the difference between cyclopentadiene and cyclopentadienyl ligands.

"Answer" The chemical formula of cyclopentadiene is C_5H_6 and it is bonded to a metal as a η^2 or η^4 ligand. The chemical formula of cyclopentadienyl is C_5H_5 and it is bonded to a metal as a η^1, η^3, or η^5 ligand.

Alkyl ligands

Alkyl or aryl transition metal compounds have M-C single bonds. In spite of many attempts over most of the course of chemical history, their isolation was unsuccessful and it was long considered that all M-C bonds were essentially unstable. Stable alkyl complexes began to be prepared gradually only from the 1950s. $Cp_2ZrCl(Pr)$,WMe_6, $CpFeMe(CO)_2$, $CoMe(py)(dmg)_2$, (dmg = dimethylglyoximato), $IrCl(X)(Et)(CO)(PPh_3)_2$, $NiEt_2(bipy)$, $PtCl(Et)(PEt_3)_2$ are some representative compounds. Among various synthetic processes so far developed, the reactions of compounds containing M-halogen bonds with main-group metal-alkyl compounds, such as a Grignard reagent or an organolithium compound, are common synthetic routes. Especially vitamin B_{12}, of which D. Hodgkin (1964 Nobel Prize) determined the structure, is known to have a very stable Co-C bond. Metal alkyl compounds which have only alkyl ligand, such as WMe_6, are called **homoleptic alkyls**.

It is gradually accepted that a major cause of the instability of alkyl complexes is the low activation energy of their decomposition rather than a low M-C bond energy. The most general decomposition path is **β elimination**. Namely, the bonding interaction of a hydrocarbon ligand with the central transition metal tends to result in the formation of a metal hydride and an olefin. Such an interaction is called an **agostic interaction**.

Although an alkyl and an aryl ligand are 1-electron ligands, they are regarded as anions when the oxidation number of the metal is counted. The hydride ligand, H, resembles the alkyl ligand in this aspect.

π allyl complexes

If an allyl group, $CH_2=CH-CH_2-$, is bonded to a metal via a carbon atom, it is a 1-electron ligand like an alkyl group. If the double bond delocalizes, three carbon atoms bond to the metal simultaneously as a 3-electron ligand. This is also an odd electron and formally anionic ligand and is stabilized by being coordinated to the metal. $Pd(C_3H_5)(Ac)(PPh_3)$, $Co(C_3H_5)_3$, *etc.* are well-known examples. Since η^1, η^2, and η^3 coordination modes are possible in the catalytic reactions of unsaturated hydrocarbons, various reactions occur.

π cyclopentadienyl complexes

The cyclopentadienyl ligand, C_5H_5, is abbreviated as Cp. C_5Me_5, in which the hydrogen atoms of Cp are replaced with methyl groups, is a useful ligand called **Cp star** and is denoted by Cp*. Ferrocene, Cp_2Fe, is a very stable orange-colored iron compound in which two cyclopentadienyl groups are bonded to iron. It was discovered independently in two laboratories, but the discoverers proposed incorrect structures. The correct structure was clarified by the group of G. Wilkinson, who won a Nobel Prize (1973). The preparation of ferrocene is usually carried out according to the following reaction path:

$$2\ C_5H_6 + 2\ Na \longrightarrow 2\ Na(C_5H_5) + H_2$$

$$FeCl_2 + 2\ Na(C_5H_5) \longrightarrow Fe(C_5H_5)_2 + 2\ NaCl$$

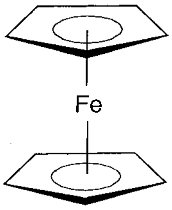


Fig. 6.16 Structure of ferrocene.

Single crystal X-ray structure analysis showed that the structure of ferrocene is an iron atom sandwiched between two C_5H_5 rings (Fig. 6.16). Five carbon atoms bond to the iron simultaneously in ferrocene, and unsaturated C-C bonds are delocalized in the five-membered rings. Since this kind of bond was not known before, it aroused interest, many derivative compounds were prepared, and a wide range of chemistry has since been studied (Table 6.6).

Table 6.6 Typical sandwich compounds (Cp = η^5-C_5H_5)

	4	5	6	7	8	9	10
4	Cp_2TiCl_2	Cp_2V	Cp_2Cr	Cp_2Mn	Cp_2Fe	Cp_2Co	Cp_2Ni
	Red	Black	Scarlet	Brown	Orange	Black	Green
	mp 230	mp 167	mp 173	mp 193	mp 174	mp 173	d.173
5	Cp_2ZrCl_2	Cp_2NbCl_2	Cp_2MoCl_2	Cp_2TcH	Cp_2Ru		
	White	Brown	Green	Yellow	Yellow		
	mp 248		d.270	mp 150	mp 200		
6	Cp_2HfCl_2	Cp_2TaCl_2	Cp_2WCl_2	Cp_2ReH	Cp_2Os		
	White	Brown	Green	Yellow	White		
	mp 234		d.250	mp 161	mp 229		

The cyclopentadienyl ligand is a 5-electron and formally anionic ligand. If only one of the five carbon atoms is bonded to a metal, it is a 1-electron ligand like an alkyl group. It becomes a 3-electron ligand in rare cases and coordinates to a metal as a π-allyl system that extends over 3 carbon atoms. The Cp group of ferrocene has reactivity analogous to that of aromatic compounds. Since the Cp group has played a significant role as a stabilizing ligand to realize the preparation of new compounds with new metal-ligand bonding modes, it can reasonably be claimed that this ligand has made the greatest contribution to organometallic chemistry of any other ligand. Although two Cp rings are bonded to the metal in parallel in ferrocene, Cp_2TiCl_2 and Cp_2MoH_2 have bent Cp ligands and they are called bent-sandwich compounds.

Olefin complexes

Zeise's salt, $K[PtCl_3(C_2H_4)]$, is the oldest known organometallic compound and was synthesized and analyzed in *ca*. 1825 by Zeise, although its coordination structure was assumed only in 1954 and confirmed by the neutron diffraction in 1975. The mode of coordination of an olefin to a transition metal is described by the Dewar-Chatt-Duncanson model and the bond between the metal and olefin is stabilized by the contribution of d_π-p_{π^*} back donation. An olefin is a 2-electron ligand and there are many olefin complexes in which the central metal is in a relatively low oxidation state.

Dienes or trienes with two or more double bonds coordinate to a metal as 4-electron or 6-electron ligands. $Fe(CO)_3(C_4H_6)$ and $Ni(cod)_2$, in which a butadiene or cyclooctadienes (cod) are coordinated to the metal, are well known examples. Since cyclooctadienes are easily eliminated from Ni(cod)$_2$, it is conveniently used for generating atomic, zero valent nickel. This complex is sometimes called **naked nickel**.

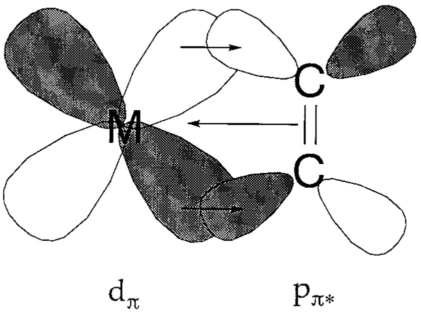


Fig. 6.17 Back-donation in olefin complexes.

Arene complexes

Aromatic compounds are 6-electron donors that coordinate to transition metals in the η^6 coordination mode with six carbon atoms. Bisbenzenechromium, $Cr(C_6H_6)_2$, is a typical example of such a compound. The compound is prepared by reducing chromium chloride in benzene and it has a sandwich structure in which a chromium atom is inserted between two benzene rings. When a benzene ligand is replaced by three carbonyls, $Cr(CO)_3(C_6H_6)$ is obtained.

18 electron rule

Counting valence electrons is of utmost importance in chemistry. Changes in the number of valence electrons has a profound influence on the bonding, structure, and reactions of a compound. Since both the metal and organic moieties are involved in organometallic compounds, counting the number of electrons becomes complicated. Hydrocarbyl ligands are classified as either neutral molecules coordinating to the metal or radicals bonding to the metal, and the radicals, such as alkyls and cyclopentadienyl, are generally called anionic ligands. Transfer of one electron from the metal to the radical ligand makes the ligand formally anionic. However, it is less confusing to consider that both the metal and the ligands are neutral when counting the number of valence electrons. The numbers of donor electrons in typical carbon ligands from this viewpoint are listed in Table 6.5. It is important to note that even in the same ligand, the number of donor electrons supplied by the ligand differs depending upon the number of ligating atoms that have coordinative interactions with the metal. For example, 1, 3 or 5 electrons can be donated from a cyclopentadienyl ligand, depending on the type of coordinative interactions with the metal.

When the total number of valence electrons of the metal and ligands is 18, a transition metal organometallic compound usually has high thermal stability. For example, $Cr(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$, $Fe(C_5H_5)_2$, $Mo(C_6H_6)(CO)_3$ *etc*. satisfy the **18 electron rule**, but the monomeric parts of $Mn_2(CO)_{10}$, $Co_2(CO)_8$ or $[Fe(C_5H_5)(CO)_2]_2$ have only 17 electrons and the extra electron comes from the partner metal by forming a metal-metal bond. Unlike the 8 electron rule in main group compounds, applicability of the 18 electron rule is limited. That is to say, it is a sufficient condition but compounds with high thermal stability are not necessarily 18 electron compounds.

Although there are many Group 6 (chromium group) through Group 9 (cobalt group) organometallic compounds with carbonyl or cyclopentadienyl ligands that satisfy the 18 electron rule, many compounds of the early transition metals (Group 3 - 5) and Group 10 (nickel group) fail to conform to this rule. For example, $W(CH_3)_6$ (12e), $TiCl_2(C_5H_5)_2$ (16e), and $IrCl_2(CO)(PPh_3)_2$ (16e), $V(CO)_6$ (17e), $Co(C_5H_5)_2$ (19e), $Ni(C_5H_5)_2$ (20e), *etc*. do not satisfy the 18 electron rule. However, the 18 electron rule provides useful clues as to the bonding modes present in a given complex. For example, $Fe(C_5H_5)_2(CO)_2$ with two pentahapto cyclopentadienyl ligands formally has 22 electrons but if one of the ligands is monohapto, the compound has 18 electrons. Structural analysis has shown that this is the actual coordination of this complex.

Exercise 6.5 Calculate the valence electron number of $CpMn(CO)_3$.
"Answer" They are a total of 18 electrons from Mn (7), Cp(5) and three CO(6).

(c) Phosphine complexes

Tertiary phosphines, PX_3, are very useful as stabilization ligands in transition metal complexes and they coordinate to the metals in relatively high to low oxidation states. Phosphines are frequently used as carbonyl or cyclopentadienyl ligands in the chemistry of organometallic complexes. PX_3 are Lewis bases and coordinate to the metal using the lone pair on phosphorus and show π-acidity when carrying substituents X including Ph, Cl, or F that have strong electron accepting properties. The electronic flexibility of PX_3 is the reason it forms so many complexes. Generally, the π-acidity becomes smaller in the order $PF_3>PCl_3>PPh_3>PR_3$. Triphenylphosphine and triethylphosphine are typical substituted phosphines. The tertiaryphosphine complexes mainly of metal halides are listed in Table 6.7. Manganese, Mn, and the early transition metals form very few phosphine complexes.

Table 6.7 Typical tertiary phosphine complexes (dmpe = 1,2-bisdimethylphosphinoethane; dppe = 1,2-bisdiphenylphosphinoethane)

	4	5	6	7
4	$[TiCl_4(PPh_3)_2]$	$[VCl_3(PMePh_2)_2]$	$[CrCl_2(dmpe)_2]$	$[Mn(CO)_4(PPh_3)]$
5	$[ZrCl_4(dppe)]$	$[NbCl_4(PEtPh_2)_2]$	$[MoCl_3(PMePh_2)_3]$	$[TcCl_3(PMe_2Ph)_3]$
6	$[HfCl_4(dppe)]$	$[TaCl_4(PEt_3)_2]$	$[WCl_4(PPh_3)_2]$	$[ReCl_3(PMe_2Ph)_3]$

	8	9	10	11
4	$[FeCl_2(PPh_3)_2]$	$[CoCl_2(PPh_3)_2]$	$[NiCl_2(PEt_3)_2]$	$[CuBr(PEt_3)]_4$
5	$[RuCl_2(PPh_3)_3]$	$[RhCl(PPh_3)_3]$	$[PdCl_2(PPh_3)_2]$	$[AgCl(PPh_3)]$
6	$[OsCl_3(PPh_3)_3]$	$[IrCl_3(PPh_3)_3]$	$[PtCl_2(PPh_3)_2]$	$[AuCl(PPh_3)]$

Many derivatives can be prepared by substituting the halogens of the phosphine complexes. A number of the complexes of polydentate phosphines with more than two coordination sites, as well as those of monodentate phosphines, have been prepared, and they are used also as stabilization ligands in hydride, alkyl, dinitrogen, and dihydrogen complexes. The complexes of rhodium or ruthenium, in which optically active phosphines are coordinated, are excellent catalysts for asymmetric synthesis.

(d) Small molecule complexes

Two or three atomic molecules, such as H_2, N_2, CO, NO, CO_2, NO_2, and H_2O, SO_2, *etc*., are called **small molecules** and the chemistry of their complexes is very important not only for basic inorganic chemistry but also for catalyst chemistry, bioinorganic chemistry, industrial chemistry, and environmental chemistry. The complexes of small molecules other than water and carbon monoxide were synthesized comparatively recently. Dihydrogen complexes in particular were reported only in 1984.

Dihydrogen complexes

The oxidative addition reaction of a hydrogen molecule, H_2, is one of the methods used to generate the M-H bond of a hydride complex. Schematically, the above reaction is written as

$$M + H_2 \longrightarrow H\text{-}M\text{-}H$$

but it was believed that there must be an intermediate complex containing a coordinated dihydrogen. The first example of a stable complex of this sort, $[W(CO)_3(H_2)(P^iPr_3)_2]$, was reported by G. Kubas in 1984 (Fig. 6.18). It was proved by the neutron diffraction that the H_2 is coordinated as an η^2 ligand by maintaining the bond between hydrogen atoms with an interatomic distance of 84 pm.

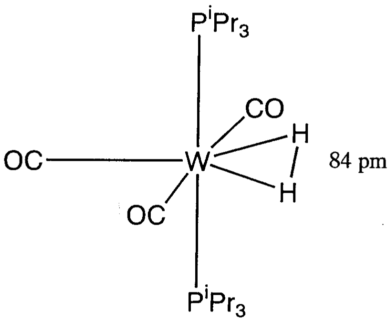


Fig. 6.18 Structure of $[W(CO)_3(H_2)(P^iPr_3)_2]$.

Once this new coordination mode was established, new dihydrogen complexes have been prepared one after another, and dozens of dihydrogen complexes are now known. Dihydrogen complexes are interesting not only from the viewpoint of bond theory but they have also greatly contributed to the study of the activation process of the hydrogen molecule.

Dinitrogen complexes

Since N_2 is isoelectronic with CO, the possible stability of dinitrogen complexes analogous in structure to carbonyl complexes was the subject of speculation for many years. These compounds generated great interest because of the parallels with the interaction and activation of nitrogen molecules on the iron catalyst used in ammonia synthesis and the nitrogen fixing enzyme nitrogenase. However, the first dinitrogen complex, $[Ru(N_2)(NH_3)_5]X_2$, was prepared by A. D. Allen (1965) unexpectedly from the reaction of a ruthenium complex and hydrazine. Subsequently, it was discovered by chance that nitrogen gas coordinates to cobalt, and $[CoH(N_2)(PPh_3)_3]$ was prepared in 1967 (Fig. 6.19). Many dinitrogen complexes have been prepared since these early beginnings.

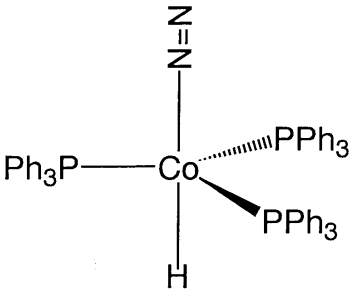


Fig. 6.19 Structure of $[CoH(N_2)(PPh_3)_3]$.

In most dinitrogen complexes, N_2 is coordinated to the metal by one nitrogen atom. That is to say, the M-N≡N bond is common and there are few complexes in which both nitrogen atoms bond to the metal in the η^2 coordination mode. In 1975, the coordinated dinitrogen in a molybdenum complex was discovered to be protonated by mineral acids to form ammonia, as decribed in the following reaction. The electrons required for the reduction are supplied by the molybdenum in a low oxidation state as this reaction shows.

$$[Mo(PMe_2Ph)_4(N_2)_2] + 6\ H^+ \longrightarrow 2\ NH_3 + N_2 + Mo(V) + \dots$$

In spite of attempts to prepare ammonia and organic nitrogen compounds from various dinitrogen complexes, no nitrogen fixation system which is equal to biological systems has yet been discovered. Ammonia synthesis is a long-established industrial process, and its parameters have been extensively studied and little room for improvement remains. However, elucidating the mechanism of the biological nitrogen fixation reaction at ordinary temperatures and pressures remains one of the major challenges of bio-inorganic chemistry.

Dioxygen complexes

Although it has long been recognized that schiff base complexes of cobalt absorb oxygen, the discovery that **Vaska's complex,** $[IrCl(CO)(PPh_3)_2]$, coordinates dioxygen reversibly to form $[IrCl(CO)(PPh_3)_2(O_2)]$ was very significant. In this complex, two oxygen atoms bond to iridium (side-on), and dioxygen has a peroxide character (O_2^{2-}). However, many superoxide (O_2^-) complexes in which only one oxygen atom is bonded to the metal are known. There are also binuclear dioxygen complexes in which O_2 bridges two metals. The relation between reversible coordination of dioxygen and its reactivity is important in relation to the behavior of dioxygen in living systems (refer to Section 8.2 (a)).

(e) Metal-metal bonds

The concept of the formation of a coordinate bond between ligands and a central metal proposed by A. Werner was the basis for the development of the chemistry of complexes. The bonding mode and structures of known complexes have become the guidepost of the preparation of a much larger number of new complexes. For most of the dinuclear or polynuclear complexes that contain two or more metals in a complex, it was sufficient to take into consideration only the bonds between the metal and ligands.

The concept of direct bonds between metals was born of the necessity of explaining the structural chemistry of the dinuclear metal carbonyls that have a partial structure with an odd number of electrons. Two $Mn(CO)_5$ units in $Mn_2(CO)_{10}$ are connected by a direct Mn-Mn bond (Fig. 6.20) without the help of bridge ligands. According to X-ray structural analysis (1963), the Mn-Mn distance of 292 pm was significantly longer than twice that of the metal radius of 127 pm but a Mn-Mn direct bond was envisaged in the absence of a bridge carbonyl ligand. This compound's diamagnetism indicates a structure with an even number of electrons (18 electrons) by sharing electrons between two d^7-Mn (17 electrons) moieties, each with five carbonyl ligands.

Similarly, it can be concluded that $Co_2(CO)_8$, with two bridging carbonyl ligands, should have a direct Co-Co bond to be compatible with its diamagnetism.

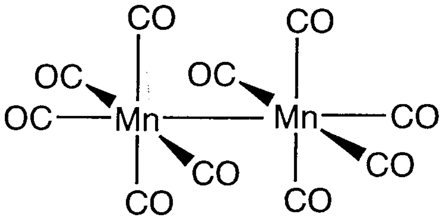


Fig. 6.20 Structure of $Mn_2(CO)_{10}$.

The concept of the single bond between metals introduced for dinuclear metal carbonyl compounds is also very useful in explaining the structure of cluster carbonyl compounds containing two or more metals. The metal-metal bond has been established today as one of the common bonding modes, together with the metal-ligand bond, present in coordination complexes. However, it is not always clear to what extent the interaction between metals exists in the polynuclear complexes which have bridging ligands. As a criterion, the bond order can be evaluated from the bond distance in standard metals (for example, in bulk metals). However, even if the bond distance between metals analyzed by

X-ray is sufficiently short, this does not prove the existence of a bond between metals unless the orbital conditions to account for such bonds are also fulfilled.

M-M multiple bonds

There are many dinuclear compounds in which the metal atoms are bound by multiple bonds with bond orders of 2 to 4. The M-M quadrupole bond was proposed first for $Re_2Cl_8^{2-}$, and this remains the best-known example (Fig. 6.21). The Re-Re distance in this compound is only 224 pm, which is unusually short compared with the Re-Re distance of 275 pm in rhenium metal. Another unusual feature is that the $ReCl_4$ units assume an **eclipsed** configuration (chlorine atoms overlap along the direction of the Re-Re bond) even though the **staggard** configuration (in which chlorine atoms do not overlap along the Re-Re bond direction) should be more stable because the distance between $ReCl_4$ units is very short, resulting in the distances between the chlorine atoms being very short (experimental value of 332 pm). As a result, the repulsive interaction between the chlorine atoms becomes strong.

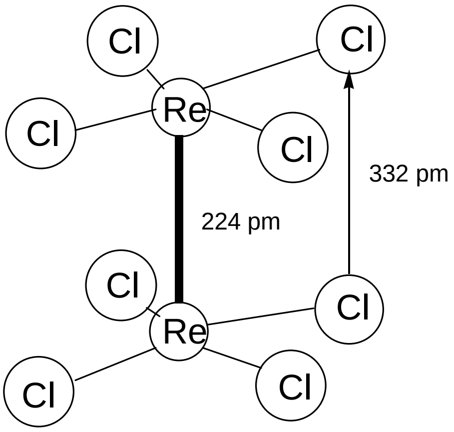


Fig. 6.21 Structure of $Re_2Cl_8^{2-}$.

F. A. Cotton explained this anomaly by introducing the concept of the delta bond between metals in 1964. Namely, if one takes the z-axis in the direction of the Re-Re bond, a σ bond is formed between the d_{z2}, the π bonds between d_{yz} and d_{xz} orbitals and the δ bond between d_{xy} orbitals among the five d orbitals. d_{x2-y2} is mainly used for the Re-Cl bond. The delta bond is formed by a weak sideway overlap of d_{xy} orbitals, when they are located perpendicular to the direction of the metal-metal bond axis and become eclipsed (Fig. 6.22). Therefore, although the δ bond is relatively weak among bonding interactions, it is sufficient to maintain the chlorine ligands in their eclipsed positions.

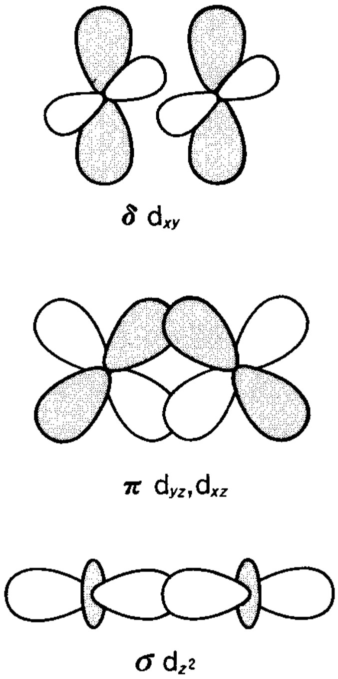


Fig. 6.22 Overlap of *d* orbitals in Re≡Re quadrupole bond.

The energy levels of the molecular orbitals of σ, π, and δ bonds decrease in this order, and the energy difference between the bonding and antibonding delta orbitals is small. Therefore, even if one electron is removed (oxidation) from $Re_2Cl_8^{2-}$, which has a quadruple bond, or one electron is added (reduction) to it, the Re-Re distance should hardly change.

The Mo(II) compound $[Mo_2(CH_3COO)_4]$ which is isoelectronic with Re (III) has a Mo-Mo quadruple bond. $[W_2Cl_9]^{3-}$ and $[W_2(NMe_2)_6]$ are examples of compounds which have the metal-metal triple bonds. Although the issue of whether such metal-metal multiple bonds really exist has been argued many times, the concept has now been established and hundreds of dinuclear compounds with metal-metal multiple bonds are known at present. Metal-metal distances determined by X-ray analysis are most useful in determining whether a metal-metal bond is a multiple one, but as in the case of metal-metal single bonds, the bond distance alone cannot be the absolute determiner and it is necessary to draw conclusions from molecular orbital calculations.

(f) Metal cluster compounds

Analysis of the structures of newly prepared polynuclear complexes that contain two or more metals was, until recently, very difficult. However, with the progress of single crystal X-ray structural analysis, our understanding of the chemistry of polynuclear complexes is progressing quickly. Metal-cluster complexes are polynuclear complexes built by three or more transition-metal atoms with bonds between the metals coordinated by ligands to form polyhedral frames, such as a triangle, a regular tetrahedron, a regular octahedron, and an icosahedron. Even if there is no strong bond between metals, as long as there is some bonding interaction, they may be included as cluster compounds.

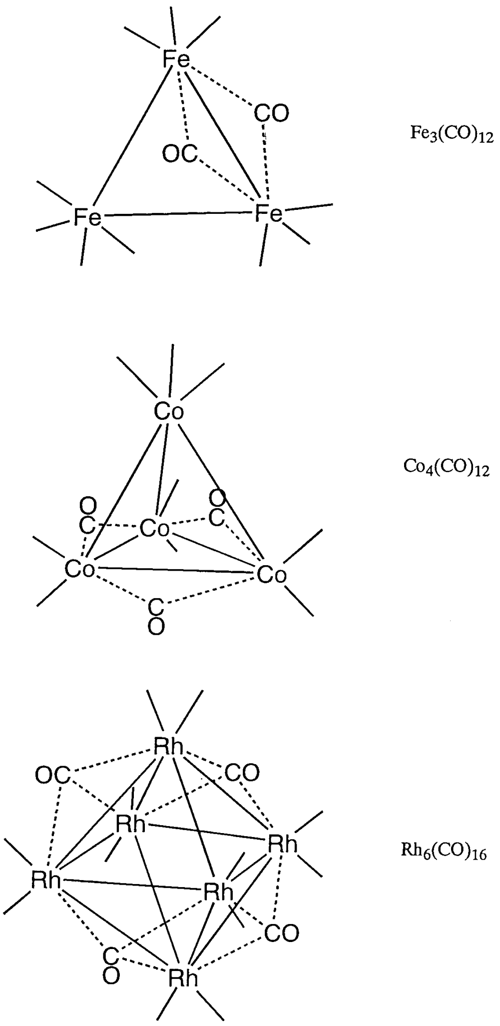


Fig. 6.23 Examples of metal cluster carbonyls (terminal carbonyl ligands are omitted for clarity.

Metal cluster complexes may be broadly classified into groups according to the general character of the associated ligands. They are low oxidation state metal clusters with π-acceptor ligands like carbonyls (CO), isonitriles (RNC) or phosphines (PR_3) and with π-donor ligands like oxygen (O), sulfur (S), chlorine (Cl) or alkoxides (OR). Many carbonyl cluster and sulfur cluster compounds have been synthesized. Carbonyl cluster compounds are obtained by heating or irradiating mononuclear carbonyl compounds. The chemical properties of cluster compounds such as $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Co_4(CO)_{12}$, $Ir_4(CO)_{12}$ or $Rh_6(CO)_{16}$ have been studied in detail (Fig. 6.23).

Since $Os_3(CO)_{12}$ forms many kinds of cluster compounds by pyrolysis, it has been used to study the skeletal structures of osmium cluster compounds and their relationship to skeletal electron numbers. A M-M bond is satisfactorily described by the 2 center 2 electron bond and the 18 electron rule is also applicable to each metal for small clusters such as a triangle and a regular tetrahedron. When clusters become large, the Wade rule that describes the relation between the structures of boranes and skeletal electron numbers, or the Lauher rule that draws the number of the bonding metal-metal orbitals for various metal polyhedral structures from the molecular orbital calculations of bare rhodium clusters without ligands, are more applicable. The relationship between the number of cluster valence electrons and the cluster's polyhedral shape as shown in Table 6.8 has contributed much to the theory of cluster chemistry.

Table 6.8 Metal frameworks and cluster valence electrons in metal cluster carbonyl compounds

Metal framework	Cluster valence electron	Example
Triangle	48	$Fe_3(CO)_{12}$
Tetrahedron	60	$Co_4(CO)_{12}$
Butterfly	62	$[Fe_4(CO)_{12}C]^{2-}$
Trigonal bipyramid	72	$Os_5(CO)_{16}$
Square pyramid	74	$Fe_5C(CO)_{15}$
Octahedron	86	$Rh_6(CO)_{16}$
Trigonal prism	90	$[Rh_6C(CO)_{15}]^{2-}$

Monovalent anions such as halogens, alkoxides, carboxylate ions, and divalent anions such as oxygen and sulfur stabilize the cluster frameworks by helping metals assume oxidation states suitable for cluster formation and connect metal fragments by bridging. Since neutral ligands such as phosphines, carbonyl, or amines can also be coordinated to metals, a variety of cluster complexes have been prepared.

The halide clusters of molybdenum, Mo_6X_{12}, tungsten, W_6X_{12}, niobium, Nb_6X_{14}, and tantalum, Ta_6X_{14}, are solid cluster compounds that have been known for many years. The octahedral metal frameworks were shown by X-ray structure analysis more than 50 years ago. The molecular cluster complexes were prepared in the 1960s from solid-state halide clusters by the reaction of ligands such as amines and phosphines, and these cluster compounds generated considerable interest for some time. New halide cluster compounds with octahedral structures have again been prepared recently and they are being studied from new perspectives. The molecular cluster complex [$Mo_6S_8L_6$] (where L is PEt_3, py, *etc.*), which has similar Mo_6 frameworks with those of the superconducting Chevrel phase compounds $MxMo_6S_6$ and their tungsten and chromium analogs have been prepared and the relationships between their structures and physical properties attract great interest (Fig. 6.24).

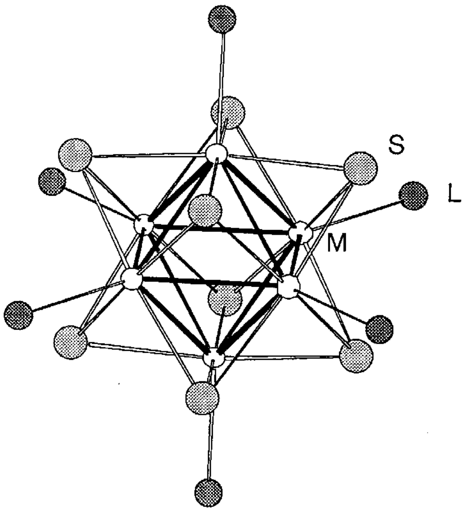


Fig. 6.24 Structure of [$Mo_6S_8L_6$].

As will be described in the Chapter on bioinorganic chemistry, clusters such as Fe_4S_4 are contained in nitrogenase, the nitrogen-fixing enzyme, and also in the active center of ferredoxins, and they play important roles in the activation of dinitrogen or multi-electron transfer reactions. Since R. H. Holm synthesized the $Fe_4S_4(SR)_4$ cluster (Fig. 6.25), our understanding of the chemistry of the iron-sulfur cluster has developed considerably.

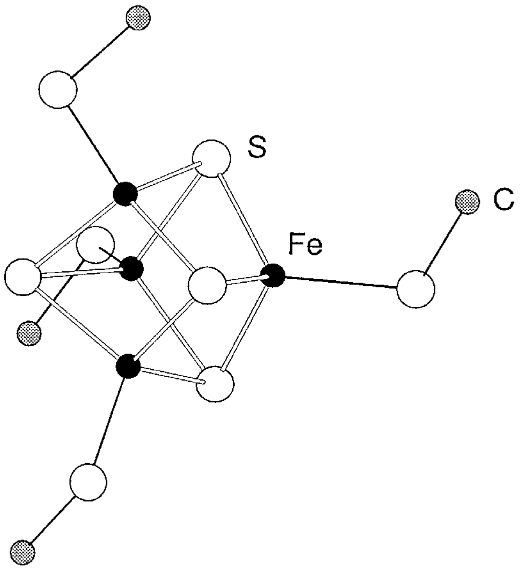


Fig. 6.25 Structure of $[Fe_4S_4(SR)_4]^{2-}$.

As the metal species of metal cluster carbonyls are in near-zero valence oxidation states, they had been expected to play a role in specific catalysis Although many organic syntheses using metal cluster compounds as catalysts have been attempted and some interesting reactions were discovered, in most cases the clusters decomposed during the reactions and they turned out to be false cluster catalysts. Despite this, there have been some examples of reactions that pass through several elementary reaction stages on the metal of the cluster. Hence, it is likely that catalytic reactions that employ the **multi-center coordination** and **multi-electron transfer** abilities of cluster compounds will be developed in the future.

Metal clusters have been helpful as models of the surfaces of bulk metals, metal oxides, or metal sulfides, and they have been useful in the study of chemisorption and successive reactions on solid surfaces. The fine metal grains which maintain the basic cluster frameworks are deposited by the pyrolysis of metal carbonyl cluster compounds chemically bonded to carriers such as silica and alumina. If used in solid catalysis, it is expected that analysis of the catalytic reaction on a metal cluster framework will be possible.

6.4 Reactions of complexes

The reactions of complexes are classified into the substitution reaction of ligands, the conversion reaction of ligands, and the redox reaction of the central metal. The substitution and redox reactions in particular have been studied in detail.

(a) Ligand substitution reaction

Ligand substitution reactions of complexes

$$L_nMX + Y \longrightarrow L_nMY + X$$

are very important for the preparation of various kinds of derivatives. The detailed conditions which complexes and ligands fulfill have been studied in order to understand their stereochemistry and attain practical rates of substitution reactions. As with other types of chemical reactions, we require an understanding of both equilibrium and reaction rates.

Formation constant

The equilibrium constant of a ligand substitution reaction is called a **formation or stability constant**. The concept and the method of computing successive formation constants were proposed by N. Bjerrum (1941). Equilibrium constants for the replacement of a hydrated ion M by other ligands L in an aqueous solution are

$$\mathrm{M} + \mathrm{L} \to \mathrm{ML} \qquad K_1 = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]}$$

$$\mathrm{ML} + \mathrm{L} \to \mathrm{ML}_2 \qquad K_2 = \frac{[\mathrm{ML}_2]}{[\mathrm{ML}][\mathrm{L}]}$$

$$\mathrm{ML}_2 + \mathrm{L} \to \mathrm{ML}_3 \qquad K_3 = \frac{[\mathrm{ML}_3]}{[\mathrm{ML}_2][\mathrm{L}]}$$

……………………..

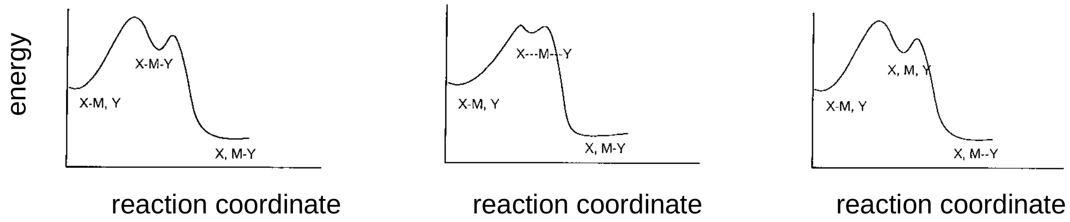
$$\mathrm{ML}_{n\text{-}1} + \mathrm{L} \to \mathrm{ML}_n \qquad K_n = \frac{[\mathrm{ML}_n]}{[\mathrm{ML}_{n\text{-}1}][\mathrm{L}]}$$

and the overall formation constant β_n is

$$\beta_n = \frac{[\mathrm{ML}_n]}{[\mathrm{M}][\mathrm{L}]^n} = K_1 K_2 K_3 \cdots K_n$$

The thermodynamic stability of a substitution product becomes larger as the formation constant increases.

On the other hand, an understanding of the effect of the leaving ligand, X, and the entering ligand, Y, on the substitution rate and on the intermediate species formed are essential to elucidate the reaction chemistry of metal complexes. It is especially useful to summarize the electronic structure of the central metals, the stereochemistry of complexes, and the correlation between the parameters representing their steric properties and the reaction rate. Generally, reaction mechanisms can be classified into associative, interchange, and dissociative mechanisms according to the differences in the intermediate state (Fig. 6.26).



(a) associative mechanism (b) interchange mechanism (c) dissociative mechanism

Fig. 6.26 The stability of the intermediate of ligand substitution.

Associative mechanism If the substitution rate of a ligand substitution of a complex is dependant upon the entering ligand, Y, coordinating to the central metal and is insensitive to the leaving ligand, X, it is presumed to take the associative mechanism which increases the coordination number. Such a substitution reaction is often seen in planar tetra-coordinate Pt(II) complexes, and the intermediate species are triangular bipyramidal penta-coordinate complexes. The reaction is first-order with respect to both the tetra-coordinate complex and Y, and is second-order as a whole. Since it is accompanied by a reduction of molecular species in the intermediate stage, thermodynamic measurements of the reaction indicate the activation entropy, ΔS, to be negative. The intermediate species in the case of the associative mechanism in hexa-coordinate complexes are hepta-coordinate complexes.

Interchange mechanism When the life of an intermediate state is very short, the reaction proceeds by the interchange mechanism, as the coordination of Y and elimination of X are considered to occur simultaneously.

Dissociative mechanism A substitution reaction that is highly sensitive to the identity of the leaving ligand, X, and practically insensitive to the identity of the entering ligand, Y, assumes the dissociative mechanism in which the coordination number decreases in the intermediate state. This is often observed in octahedral hexa-coordinate complexes, and the intermediate states are penta-coordinate complexes that form by the elimination of X. As the elimination is accompanied by an increase of molecular species in the intermediate stage, the entropy of activation, ΔS, becomes positive.

Exercise 6.6 The order of the rate of ligand substitution of Pt(II) complexes is $H_2O<Cl^-<I^-<PR_3<CN^-$ for entering ligands. Which mechanism, associative or dissosiative, do the substitutions take?

"Answer" Since they are dependent on the entering ligands, the associative mechanism is more likely.

Trans effect In square-planar tetra-coordinate complexes typically of Pt(II), the ligand trans to the leaving ligand X governs the substitution rate. This is called the **trans effect**. The substitution rate increases as the σ donor or π acceptor ability of the trans ligand becomes larger in the order of $NH_3 < Cl^- < Br^- < I^- < NCS^- < PR_3 < CN^- < CO$.

An analogous effect may also be seen in octahedral hexa-coordinate complexes, although the effect is usually relatively small.

The H_2O exchange rate in aqua ions Inert, intermediate, and labile are classification of the exchange rate proposed by H. Taube (1952). The exchange rate of aqua ions (ions coordinated by water molecules) of main-group and transition metals differ greatly depending upon the identity of the metal species. Since the rate of water ligand exchange is well correlated with the exchange rates of other ligands, it is useful for general comparison of the exchange rates in the complexes of different metal ions. For alkali and alkaline earth metals, the exchange rates are very high (10^5-10^9 s^{-1}), and the complexes of these metals are classified as labile. As the dissociative mechanism is generally found in these cases, ions with smaller ionicity and of larger size attract water ligands less and their exchange rates becomes higher. In Group 12 metal ions Zn^{2+}, Cd^{2+}, Hg^{2+}, Group 13 metal ions Al^{3+}, Ga^{3+}, $In3^+$ and Group 3 metal ions Sc^{3+}, Y^{3+}, rapid water ligand exchange takes place by a dissociative mechanism.

On the other hand, the exchange rates of M (II) ions in *d* block transition metal ions is medium (10-10^4 s^{-1}), and that of M (III) ions are lower still. The rates of d^3 Cr^{3+} and d^6 Co^{3+} are notably slow (10^{-1}-10^{-9} s^{-1}), and their complexes are termed inert. There has been a great deal of study of ligand-exchange reactions. The exchange rates are smaller the larger the ligand field stabilization energy. Therefore, the ligand-exchange rates of 4*d* and 5*d* transition metal complexes are generally slow.

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Test tube experiments

Easy chemical or biological reactions performed in test tubes are sometimes called test tube experiments. Solutions in test tubes are mixed at room temperature in air and the mixture is shaken to observe a color change or formation of precipitates and the results of the reactions are speculated on. University professors occasionally attempt these sorts of experiments. Although easy, these simple experiments show only the effects of visible light absorption and solubility. However, since even great discoveries can be born from such experiments, they should not be dismissed.

H. Taube wrote that he found a hint of the inner-sphere electron transfer mechanism from test tube experiments. He mixed Cr^{2+}(aq) and I_2 in a test tube in order to clarify the oxidation of Cr^{2+}(aq) and observed the change of color to the one characteristic of $[Cr(H_2O)_6]^{3+}$ via green. The green color is due to $[(H_2O)_5CrI]^{2+}$ which is unstable and changes to $[Cr(H_2O)_6]^{3+} + I^-$. He assumed that this was due to the formation of a Cr-I bond before Cr(II) was oxidized by I_2. Subsequently, he performed another test tube experiment using $[(NH_3)_5CoCl]^{2+}$ as an oxidant and found that Cr^{2+}(aq) was converted into $[Cr(H_2O)_6]^{3+}$ via green $[(H_2O)_5CrCl]^{2+}$. This reaction established the inner-sphere electron transfer mechanism in which a Co-Cl-Cr bridge forms between Co^{3+} and Cr^{2+} and led to the Nobel Prize in a later year.

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(b) Redox reactions

The oxidation number of the central metal in a transition-metal compound can vary in a few steps from low to high. Namely, the oxidation state of a compound is changeable by redox reactions. As a consequence of this, the bond distance and the bond angle between the metal and coordinating elements, or between metals, change, and at times the whole structure of a complex can be distorted remarkably or the compound may even decompose.

The reactions of a metal compound with various reducing or oxidizing agents are also very important from the viewpoint of synthetic chemistry. Especially, reduction reactions are used in the preparation of organometallic compounds, such as metal carbonyls or cluster compounds.

Meanwhile, the study of electron transfer between complexes, especially the redox reactions of transition metal complexes, has developed. Taube won the Nobel Prize (1983) for the study of electron transfer reactions in transition metal complexes, classifying such reactions into two mechanisms. The mechanism of electron transfer in which a bridging ligand is shared between two metals is called the **inner-sphere mechanism**, and the one involving a direct transfer of electrons between two metals without a bridging ligand is called the **outer-sphere mechanism**.

Inner-sphere mechanism When $[CoCl(NH_3)_5]^{2+}$ is reduced by $[Cr(OH_2)_6]^{2+}$, an intermediate complex, $[(NH_3)_5Co\text{-}Cl\text{-}Cr(OH_2)_5]^{4+}$, is formed in which the chlorine atom forms a bridge between cobalt and chromium. As a result of an electron transfer from chromium to cobalt through chlorine, $[Co(NH_3)_5Cl]^{+}$, in which cobalt is reduced from a trivalent to a divalent oxidation state and $[Cr(OH_2)_6]^{3+}$, in which chromium is oxidized from a divalent to a trivalent oxidation state, are formed. This kind of reaction is a redox reaction via the inner-sphere mechanism. The anions other than halogens suitable for such bridge formation are SCN^-, N_3^-, CN^-, *etc*. .

Outer-sphere mechanism When $[Fe(phen)_3]^{3+}$ (phen is orthophenanthroline) is reduced by $[Fe(CN)_6]^{4-}$, no ligand bridge forms between the metals and an electron moves from the HOMO of Fe(II) to the LUMO of Fe(III) in a very short and direct contact between the two complexes. As the result of the electron transfer, $[Fe(phen)_3]^{2+}$ and $[Fe(CN)_6]^{3-}$ form. This kind of reaction is a redox one via the outer-sphere mechanism, and is characteristic of a complex system that has a very slow ligand substitution rate compared with the speed of electron transfer, especially in systems that have the same ligands but different oxidation-numbers, for example, $[Fe(CN)_6]^{3-}$ - $[Fe(CN)_6]^{4-}$ has a high rate of electron transfer. R. A. Marcus won the Nobel Prize (1992) for his study of this outer-sphere electron transfer mechanism.

Problem

6.1 Which cavity, either the octahedral or tetrahedral one, in an array of oxygen atoms do Fe^{2+} ions tend to occupy in iron oxide Fe_3O_4 containing both Fe^{2+} and Fe^{3+} ions?

6.2 Describe a method of preparing *trans*-$[PtCl(Et)(PEt_3)_2]$.

6.3 Propose mononuclear and dinuclear metal complexes containing cyclopentadienyl and carbonyl ligands that satisfy the 18-electron rule.

6.4 Devise a method of selective syntheses of *cis*-$[PtCl_2(NH_3)_2]$ and *trans*-$[PtCl_2(NH_3)_2]$ using the trans effect.

6.5 How can it be proven that the reduction reaction of $[CoCl(NH_3)_5]^{2+}$ by $[Cr(OH_2)_6]^{2+}$ proceeds by the inner-sphere electron transfer mechanism?