d-Metal complexes play an important role in inorganic chemistry. In this chapter, we discuss the nature of ligand–metal bonding in terms of two theoretical models. We start with the simple but useful crystal-field theory, which is based on an electrostatic model of the bonding, and then progress to the more sophisticated ligand-field theory. Both theories invoke a parameter, the ligand-field splitting parameter, to correlate spectroscopic and magnetic properties. We then examine the electronic spectra of complexes and see how ligand-field theory allows us to interpret the energies and intensities of electronic transitions.

We now examine in detail the bonding, electronic structure, electronic spectra, and magnetic properties of the d-metal complexes introduced in Chapter 7. The striking colours of many d-metal complexes were a mystery to Werner when he elucidated their structures, and the origin of the colours was clarified only when the description of electronic structure in terms of orbitals was applied to the problem in the period from 1930 to 1960. Tetrahedral and octahedral complexes are the most important, and the discussion begins with them.

Electronic structure

There are two widely used models of the electronic structure of d-metal complexes. One (‘crystal-field theory’) emerged from an analysis of the spectra of d-metal ions in solids; the other (‘ligand-field theory’) arose from an application of molecular orbital theory. Crystal-field theory is more primitive, and strictly speaking it applies only to ions in crystals; however, it can be used to capture the essence of the electronic structure of complexes in a straightforward manner. Ligand-field theory builds on crystal-field theory: it gives a more complete description of the electronic structure of complexes and accounts for a wider range of properties.

20.1 Crystal-field theory

In crystal-field theory, a ligand lone pair is modelled as a point negative charge (or as the partial negative charge of an electric dipole) that repels electrons in the d orbitals of the central metal ion. The theory concentrates on the resulting splitting of the d orbitals into groups with different energies, and uses that splitting to rationalize and correlate the optical spectra, thermodynamic stability, and magnetic properties of complexes.

(a) Octahedral complexes

Key points: In the presence of an octahedral crystal field, d orbitals are split into a lower-energy triply degenerate set (t_{2g}) and a higher-energy doubly degenerate set (e_{g}) separated by an energy \( \Delta_{J} \); the ligand-field splitting parameter increases along a spectrochemical series of ligands and varies with the identity and charge of the metal atom.

In the model of an octahedral complex used in crystal-field theory, six point negative charges representing the ligands are placed in an octahedral array around the central metal ion. These charges (which we shall refer to as the ‘ligands’) interact strongly with the
central metal ion, and the stability of the complex stems in large part from this attractive interaction between opposite charges. However, there is a much smaller but very important secondary effect arising from the fact that electrons in different d orbitals interact with the ligands to different extents. Although this differential interaction is little more than about 10 per cent of the overall metal–ligand interaction energy, it has major consequences for the properties of the complex and is the principal focus of this section.

Electrons in \( d_{z^2} \) and \( d_{x^2-y^2} \) orbitals (which are of symmetry type \( e_g \) in \( O_h \); Section 6.1) are concentrated close to the ligands, along the axes, whereas electrons in \( d_{xy}, d_{yz}, \) and \( d_{zx} \) orbitals (which are of symmetry type \( t_{2g} \)) are concentrated in regions that lie between the ligands (Fig. 20.1). As a result, the former are repelled more strongly by the negative charge on the ligands than the latter and lie at a higher energy. Group theory shows that the two \( e_g \) orbitals have the same energy (although this is not readily apparent from drawings), and that the three \( t_{2g} \) orbitals also have the same energy. This simple model leads to an energy-level diagram in which the three degenerate \( t_{2g} \) orbitals lie below the two degenerate \( e_g \) orbitals (Fig. 20.2). The separation of the two sets of orbitals is called the ligand-field splitting parameter, \( \Delta_0 \) (where the subscript \( O \) signifies an octahedral crystal field).

**A note on good practice** In the context of crystal-field theory, the ligand-field splitting parameter should be called the crystal-field splitting parameter, but we use ligand-field splitting parameter to avoid a proliferation of names.

The energy level that corresponds to the hypothetical spherically symmetrical environment (in which the negative charge due to the ligands is evenly distributed over a sphere instead of being localized at six points) defines the barycentre of the array of levels, with the two \( e_g \) orbitals lying at \( \pm \Delta_0 \) above the barycentre and the three \( t_{2g} \) orbitals lying at \( \pm \frac{1}{3} \Delta_0 \) below it. As in the representation of the configurations of atoms, a superscript is used to indicate the number of electrons in each set, for example \( t_{2g}^2 \).

The simplest property that can be interpreted by crystal-field theory is the absorption spectrum of a one-electron complex. Figure 20.3 shows the optical absorption spectrum of the \( d^1 \) hexaquatitanium(III) ion, \( [\text{Ti(OH}_2)_6]^{3+} \). Crystal-field theory assigns the first absorption maximum at 493 nm (20 300 cm\(^{-1}\)) to the transition \( e_g \leftarrow t_{2g} \) and identifies 20 300 cm\(^{-1}\) with \( \Delta_0 \) for the complex. It is not so straightforward to obtain values of \( \Delta_0 \) for complexes with more than one d electron because the energy of a transition then depends not only on orbital energies but also on the electron–electron repulsion energies. This aspect is treated more fully in Section 20.4 and the results from the analyses described there have been used to obtain the values of \( \Delta_0 \) in Table 20.1.
The ligand-field splitting parameter, $\Delta_\alpha$, varies systematically with the identity of the ligand. For instance, in the series of complexes $[\text{CoX(NH}_3\text{)}]^{2+}$ with $X = \text{I}^-$, Br$^-$, Cl$^-$, H$_2$O, and NH$_3$, the colours range from purple (for X = I$^-$) through pink (for Cl$^-$) to yellow (with NH$_3$). This sequence indicates that the energy of the lowest energy electronic transition (and therefore $\Delta_\alpha$) increases as the ligands are varied along the series. The same order is followed regardless of the identity of the metal ion. Thus ligands can be arranged in a spectrochemical series, in which the members are arranged in order of increasing energy of transitions that occur when they are present in a complex:

$\text{I}^- < \text{Br}^- < \text{S}^2^- < \text{SCN}^- < \text{Cl}^- < \text{NO}_2^- < \text{N}^+$ < F$^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{CH}_3\text{CN} < \text{py} < \text{NH}_3 < \text{en} < \text{bpy} < \text{phen} < \text{NO}_2^- < \text{PPh}_3^- < \text{CN}^- < \text{CO}$

(The donor atom in an ambidentate ligand is underlined.) Thus, the series indicates that, for the same metal, the optical absorption of the cyano complex will occur at higher energy than that of the corresponding chlorido complex. A ligand that gives rise to a high-energy transition (such as CO) is referred to as a strong-field ligand, whereas one that gives rise to a low-energy transition (such as Br$^-$) is referred to as a weak-field ligand. Crystal-field theory alone cannot explain these strengths, but ligand-field theory can, as we shall see in Section 20.2.

The ligand-field strength also depends on the identity of the central metal ion, the order being approximately:

$\text{Mn}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{V}^{2+} < \text{Fe}^{3+} < \text{Co}^{3+} < \text{Mo}^{3+} < \text{Rh}^{3+} < \text{Ru}^{3+} < \text{Pd}^{4+} < \text{Ir}^{3+} < \text{Pt}^{4+}$

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

(b) Ligand-field stabilization energies

Key point: The ground-state configuration of a complex reflects the relative values of the ligand-field splitting parameter and the pairing energy. For 3d$^1$ species with $n = 4–7$, high-spin and low-spin complexes occur in the weak-field and strong-field cases, respectively. Complexes of 4d- and 5d-series metals are typically low-spin.

Because the d orbitals in a complex do not all have the same energy, the ground-state electron configuration of a complex is no longer immediately obvious. To predict it, we use the
The ground-state electron configurations of $3d^4$, $3d^5$, and $3d^{10}$ complexes are unambiguous because there is no competition between the additional stabilization achieved by occupying the $t_{2g}$ orbitals and the pairing energy; the configurations are $t_{2g}^4$, $t_{2g}^5$, and $t_{2g}^9$, respectively, with each electron in a separate orbital. As remarked above, there are two possible configurations for $3d^4$ complexes; the same is true of $3d^9$ complexes in which $n = 5, 6$, or $7$. In the strong-field case, the lower orbitals are occupied preferentially and in the weak-field case, electrons avoid the pairing energy by occupying the upper orbitals.

When alternative configurations are possible, the species with the smaller number of parallel electron spins is called a low-spin complex, and the species with the greater number of parallel electron spins is called a high-spin complex. As we have noted, an octahedral $3d^4$ complex is likely to be low-spin if the ligand field is strong but high-spin if the field is weak (Fig. 20.4); the same applies to $3d^3$, $3d^8$, and $3d^7$ complexes:

<table>
<thead>
<tr>
<th>Weak-field ligands</th>
<th>Strong-field ligands</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Configuration</strong></td>
<td><strong>Unpaired electrons</strong></td>
</tr>
<tr>
<td>---------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>$3d^4$</td>
<td>$t_{2g}^4 e_{g}^0$</td>
</tr>
<tr>
<td>$3d^5$</td>
<td>$t_{2g}^5 e_{g}^0$</td>
</tr>
<tr>
<td>$3d^6$</td>
<td>$t_{2g}^6 e_{g}^0$</td>
</tr>
<tr>
<td>$3d^7$</td>
<td>$t_{2g}^7 e_{g}^0$</td>
</tr>
</tbody>
</table>

The ground-state electron configurations of $3d^4$, $3d^5$, and $3d^{10}$ complexes are unambiguous and the configurations are $t_{2g}^4 e_{g}^0$, $t_{2g}^5 e_{g}^0$, and $t_{2g}^9 e_{g}^0$.

In general, the net energy of a $t_{2g}^4 e_{g}^0$ configuration relative to the barycentre, without taking the pairing energy into account, is $(0.4x - 0.6y)\Delta_{op}$. Pairing energies need to be taken

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**A note on good practice** The term crystal-field stabilization energy (CFSE) is widely used in place of LFSE, but strictly speaking the term is appropriate only for ions in crystals.

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d-orbital energy level diagram shown in Fig. 20.2 as a basis for applying the building-up principle. That is, we identify the lowest energy configuration subject to the Pauli exclusion principle (a maximum of two electrons in an orbital) and (if more than one degenerate orbital is available) to the requirement that electrons first occupy separate orbitals and do so with parallel spins.

First, we consider complexes formed by the $3d$-series elements. In an octahedral complex, the first three $d$ electrons of a $3d^n$ complex occupy separate $t_{2g}$ orbitals, and do so with parallel spins. For example, the ions $\text{Ti}^{2+}$ and $\text{V}^{2+}$ have electron configurations $3d^4$ and $3d^3$, respectively. The $d$ electrons occupy the lower $t_{2g}$ orbitals as shown in (1) and (2), respectively. The energy of a $t_{2g}$ orbital relative to the barycentre of an octahedral ion is $-0.4\Delta_{op}$, and the complexes are stabilized by $2 \times (0.4\Delta_{op}) = 0.8\Delta_{op}$ (for $\text{Ti}^{2+}$) and $3 \times (0.4\Delta_{op}) = 1.2\Delta_{op}$ (for $\text{V}^{2+}$). This additional stability, relative to the barycentre is called the ligand-field stabilization energy (LFSE).

The next electron needed for the $3d^4$ ion $\text{Cr}^{3+}$ may enter one of the $t_{2g}$ orbitals and pair with the electron already there (3). However, if it does so, it experiences a strong Coulombic repulsion, which is called the pairing energy, $P$. Alternatively, the electron may occupy one of the $e_g$ orbitals (4). Although the pairing penalty is now avoided, the orbital energy is higher by $\Delta_{op}$. In the first case ($t_{2g}^4$), there is a stabilisation of $1.6\Delta_{op}$, countered by the pairing energy of $P$, giving a net LFSE of $1.6\Delta_{op} - P$. In the second case ($t_{2g}^4 e_g^1$), the LFSE is $3 \times (0.4\Delta_{op}) = 0.6\Delta_{op}$ as there is no pairing energy to consider. Which configuration is adopted depends on which of $1.6\Delta_{op} - P$ and $0.6\Delta_{op}$ is the larger.

If $\Delta_{op} < P$, which is called the weak-field case, a lower energy is achieved when the upper orbital is occupied to give the configuration $t_{2g}^4 e_g^1$. If $\Delta_{op} > P$, which is called the strong-field case, a lower energy is achieved by occupying only the lower orbitals despite the cost of the pairing energy. The resulting configuration is now $t_{2g}^4$. For example, [Cr(OH)$_6$]$^{2+}$ has the ground-state configuration $t_{2g}^4 e_g^1$ whereas [Cr(CN)$_6$]$^{2+}$, with relatively strong-field ligands (as indicated by the spectrochemical series), has the configuration $t_{2g}^4$. In the weak-field case, all the electrons occupy different orbitals and have parallel spins. The resulting spin correlation effect (the tendency of electrons of the same spin to avoid each other) helps to offset the cost of occupying orbitals of higher energy.

The ground-state electron configurations of $3d^1$, $3d^2$, and $3d^3$ complexes are unambiguous because there is no competition between the additional stabilization achieved by occupying the $t_{2g}$ orbitals and the pairing energy; the configurations are $t_{2g}^1$, $t_{2g}^2$, and $t_{2g}^3$, respectively, with each electron in a separate orbital. As remarked above, there are two possible configurations for $3d^4$ complexes; the same is true of $3d^9$ complexes in which $n = 5, 6$, or $7$. In the strong-field case, the lower orbitals are occupied preferentially and in the weak-field case, electrons avoid the pairing energy by occupying the upper orbitals.

When alternative configurations are possible, the species with the smaller number of parallel electron spins is called a low-spin complex, and the species with the greater number of parallel electron spins is called a high-spin complex. As we have noted, an octahedral $3d^4$ complex is likely to be low-spin if the ligand field is strong but high-spin if the field is weak (Fig. 20.4); the same applies to $3d^3$, $3d^8$, and $3d^7$ complexes:
into account only for pairing that is additional to the pairing that occurs in a spherical field. Figure 20.5 shows the case of a d⁶ ion. In both the free ion and the high-spin complex two electrons are paired, whereas in the low-spin case all six electrons occur as three pairs. Thus we do not need to consider the pairing energy in the high-spin case, as there is no additional pairing. There are two additional pairings in the low-spin case, so two pairing energy contributions must be taken into account. In general, high-spin complexes always have the same number of unpaired electrons as in a spherical field (free ion), and we therefore do not need to consider pairing energies for high-spin complexes. Table 20.2 lists the values for the LFSE of the various configurations of octahedral ions, with the appropriate pairing energies taken into account for the low-spin complexes. Remember that the LFSE is generally only a small fraction of the overall interaction between the metal atom and the ligands.

The strength of the crystal field (as measured by the value of ΔO) and the spin-pairing energy (as measured by P) depend on the identity of both the metal and the ligand, so it is not possible to specify a universal point in the spectrochemical series at which a complex changes from high spin to low spin. For 3d-metal ions, low-spin complexes commonly occur for ligands that are high in the spectrochemical series (such as CN⁻) and high-spin complexes are common for ligands that are low in the series (such as F⁻). For octahedral d⁶ complexes with n = 1–3 and 8–10 there is no ambiguity about the configuration (see Table 20.2), and the designations high-spin and low-spin are not used.

As we have seen, the values of ΔO for complexes of 4d- and 5d-series metals are typically higher than for the 3d-series metals. Pairing energies for the 4d- and 5d-series metals tend to be lower than for the 3d-series metals because the orbitals are less compact and electron-electron repulsions correspondingly weaker. Consequently, complexes of these metals generally have electron configurations that are characteristic of strong crystal fields and typically have low spin. An example is the 4d⁶ complex [RuCl₆]²⁻, which has a t²⁶ configuration, which is typical of a strong crystal field despite Cl⁻ being low in the spectrochemical series. Likewise, [Ru(ox)₆]³⁻ has the low-spin configuration t²⁶ whereas [Fe(ox)₆]³⁻ has the high-spin configuration t²⁶ e²⁶.

**Table 20.2** Ligand-field stabilization energies for octahedral complexes*

<table>
<thead>
<tr>
<th>d⁶</th>
<th>Example</th>
<th>N (high spin)</th>
<th>LFSE/ΔO</th>
<th>N (low spin)</th>
<th>LFSE/ΔO</th>
</tr>
</thead>
<tbody>
<tr>
<td>d⁶</td>
<td>Ti⁴⁺</td>
<td>3</td>
<td>1.2</td>
<td>2</td>
<td>1.6 – P</td>
</tr>
<tr>
<td>d⁵</td>
<td>V⁴⁺</td>
<td>2</td>
<td>0.8</td>
<td>0</td>
<td>2.0 – 2P</td>
</tr>
<tr>
<td>d⁴</td>
<td>Cr⁵⁺</td>
<td>4</td>
<td>0.6</td>
<td>0</td>
<td>2.4 – 2P</td>
</tr>
<tr>
<td>d⁴</td>
<td>Mn⁶⁺</td>
<td>5</td>
<td>0.4</td>
<td>0</td>
<td>1.8 – P</td>
</tr>
<tr>
<td>d⁴</td>
<td>Fe⁷⁺</td>
<td>3</td>
<td>0.8</td>
<td>1</td>
<td>1.8 – P</td>
</tr>
<tr>
<td>d⁴</td>
<td>Ni⁶⁺</td>
<td>2</td>
<td>1.2</td>
<td>3</td>
<td>1.2</td>
</tr>
<tr>
<td>d⁴</td>
<td>Cu⁷⁺</td>
<td>1</td>
<td>0.6</td>
<td>0</td>
<td>1.2</td>
</tr>
<tr>
<td>d⁴</td>
<td>Cu⁺</td>
<td>1</td>
<td>0.6</td>
<td>0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

* N is the number of unpaired electrons.

**EXAMPLE 20.1 Calculating the LFSE**

Determine the LFSE for the following octahedral ions from first principles and confirm the value matches those in Table 20.2: (a) d⁵, (b) high-spin d⁵, (c) high-spin d⁴, (d) low-spin d⁵, (e) d⁶.

**Answer** We need to consider the total orbital energy in each case and, when appropriate, the pairing energy. (a) A d⁶ ion has configuration t²⁶ (no pairing of electrons) and therefore LFSE = 3 × (0.4ΔO) = 1.2ΔO; (b) A high spin d⁵ ion has configuration t²⁶ e²⁶ (no pairing of electrons) therefore LFSE = 3 × (0.4ΔO) – 2 × (0.6ΔO) = 0. (c) A high-spin d⁶ ion has configuration t²⁶ e²⁶ with the pairing of two electrons. However,
since those two electrons would be paired in a spherical field there is no additional pairing energy to be concerned with. Therefore LFSE = 4 × (0.4ΔS) − 2 × (0.6ΔS) = 0.4ΔS. (d) A low-spin d^6 ion has configuration t_2g^6 with the pairing of three pairs of electrons. However, since one pair of electrons would be paired in a spherical field the additional pairing energy is 2P. Therefore LFSE = 6 × (0.4ΔS) − 2P = 2.4ΔS − 2P. (e) A d^3 ion has configuration t_2g^3e^1 with the pairing of four pairs of electrons. However, since all four pairs of electrons would be paired in a spherical field there is no additional pairing energy. Therefore LFSE = 6 × (0.4ΔS) − 3 × (0.6ΔS) = 0.6ΔS.

Selftest 20.1 What is the LFSE for both high- and low-spin d^3 configurations?

(c) Magnetic measurements

Key points: Magnetic measurements are used to determine the number of unpaired spins in a complex and hence to identify its ground-state configuration. A spin-only calculation may fail for low-spin d^9 and for high-spin 3d^6 and 3d^7 complexes.

The experimental distinction between high-spin and low-spin octahedral complexes is based on the determination of their magnetic properties. Compounds are classified as diamagnetic if they are repelled by a magnetic field and paramagnetic if they are attracted by a magnetic field. The two classes are distinguished experimentally by magnetometry (Chapter 8). The magnitude of the paramagnetism of a complex is commonly reported in terms of the magnetic dipole moment it possesses: the higher the magnetic dipole moment of the complex, the greater the paramagnetism of the sample.

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

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

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

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

A measurement of the magnetic moment of a d-block complex can usually be interpreted in terms of the number of unpaired electrons it contains, and hence the measurement can be used to distinguish between high-spin and low-spin complexes. For example, magnetic measurements on a d^6 complex easily distinguish between a high-spin t_2g^6e^2 (N = 4, S = 2, $\mu = 4.90\mu_B$) configuration and a low-spin t_2g^6 (N = 0, S = 0, $\mu = 0$) configuration.

The spin-only magnetic moments for some electron configurations are listed in Table 20.3 and compared there with experimental values for a number of 3d complexes. For most 3d complexes (and some 4d complexes), experimental values lie reasonably close to spin-only predictions, so it becomes possible to identify correctly the number of unpaired electrons and assign the ground-state configuration. For instance, [Fe(OH)₆]³⁺ is paramagnetic with a magnetic moment of 5.9$\mu_B$. As shown in Table 20.3, this value is consistent with there being five unpaired electrons (N = 5 and S = 5/2), which implies a high-spin t_2g^3e^3 configuration.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Electron configuration</th>
<th>$S$</th>
<th>$\mu/\mu_B$ Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti³⁺</td>
<td>t_2g^6</td>
<td>⁵⁄₂</td>
<td>1.73</td>
<td>1.7−1.8</td>
</tr>
<tr>
<td>V³⁺</td>
<td>t_2g^5e^1</td>
<td>⁵⁄₂</td>
<td>2.83</td>
<td>2.7−2.9</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>t_2g^4e¹</td>
<td>⁵⁄₂</td>
<td>3.87</td>
<td>3.8</td>
</tr>
<tr>
<td>Mn³⁺</td>
<td>t_2g^3e³</td>
<td>⁵⁄₂</td>
<td>4.90</td>
<td>4.8−4.9</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>t_2g^1e⁵</td>
<td>⁵⁄₂</td>
<td>5.92</td>
<td>5.9</td>
</tr>
</tbody>
</table>
The interpretation of magnetic measurements is sometimes less straightforward than this example might suggest. For example, the potassium salt of [Fe(CN)]

3+ has \( \mu = 2.3\mu_B \) which is between the spin-only values for one and two unpaired electrons \( (1.7\mu_B \text{ and } 2.8\mu_B) \). In this case, the spin-only assumption has failed because the orbital contribution to the magnetic moment is substantial.

For orbital angular momentum to contribute, and hence for the paramagnetism to differ significantly from the spin-only value, there must be one or more unfilled or half-filled orbitals similar in energy to the orbitals occupied by the unpaired spins and of the appropriate symmetry (one that is related to the occupied orbital by rotation round the direction of the applied field). If that is so, the applied magnetic field can force the electrons to circulate around the metal ion by using the low-lying orbitals and hence it generates orbital angular momentum and a corresponding orbital contribution to the total magnetic moment (Fig. 20.6). Departure from spin-only values is generally large for low-spin 3d

5 and for high-spin 3d

8 complexes. It is also possible for the electronic state of the metal ion to change (for example with temperature), leading to a change from high-spin to low-spin and a change in the magnetic moment. Such complexes are referred to as spin-crossover complexes and are discussed in more detail, together with the effects of cooperative magnetism, in Sections 20.8 and 20.9.

EXAMPLE 20.2 Inferring an electron configuration from a magnetic moment

The magnetic moment of a certain octahedral Co(II) complex is 4.0\( \mu_B \). What is its d-electron configuration?

**Answer** We need to match the possible electron configurations of the complex with the observed magnetic dipole moment. A Co(II) complex is \( d^7 \). The two possible configurations are \( t^6 \) \( e^1 \) (high spin, \( N = 3, S = \frac{3}{2} \)) with three unpaired electrons or \( t^5 \) \( e^2 \) (low spin, \( N = 1, S = 0 \)) with one unpaired electron. The spin-only magnetic moments are 3.87\( \mu_B \) and 1.73\( \mu_B \), respectively (see Table 20.3). Therefore, the only consistent assignment is the high-spin configuration \( t^5 \) \( e^2 \).

**Self-test 20.2** The magnetic moment of the complex [Mn(NCS)]

6

3+ is 6.06\( \mu_B \). What is its electron configuration?

(d) Thermochemical correlations

**Key point:** The experimental variation in hydration enthalpies reflects a combination of the variation in radii of the ions (the linear trend) and the variation in LFSE (the saw-tooth variation).

The concept of ligand-field stabilization energy helps to explain the double-humped variation in the hydration enthalpies of the high-spin octahedral 3d-metal M

2+ ions (Fig. 20.7). The nearly linear increase across a period shown by the filled circles represents the increasing strength of the bonding between H

2+ O ligands and the central metal ion as the ionic radii decrease from left to right across the period. The deviation of hydration enthalpies from a straight line reflects the variation in the ligand-field stabilization energies. As Table 20.2 shows, the LFSE increases from \( d^1 \) to \( d^4 \), decreases again to \( d^7 \), then rises to \( d^8 \). The filled circles in Fig. 20.7 were calculated by subtracting the high-spin LFSE from \( \Delta_{\text{hf}}H \) by using the spectroscopic values of \( \Delta_{\text{hf}} \) in Table 20.1. We see that the LFSE calculated from spectroscopic data accounts for the additional ligand binding energy for the complexes shown in the illustration.

**EXAMPLE 20.3 Using the LFSE to account for thermochemical properties**

The oxides of formula MO, which all have octahedral coordination of the metal ions in a rocksalt structure, have the following lattice enthalpies:

| Metal | \( \Delta_{\text{hyd}}H^\circ \) (kJ mol

\(^{-1}\) | \( \Delta_{\text{obs}}H^\circ \) (kJ mol

\(^{-1}\) |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>3460</td>
</tr>
<tr>
<td>Ti</td>
<td>3878</td>
</tr>
<tr>
<td>V</td>
<td>3913</td>
</tr>
<tr>
<td>Mn</td>
<td>3810</td>
</tr>
</tbody>
</table>

Account for the trends in terms of the LFSE.

**Answer** We need to consider the simple trend that would be expected on the basis of trends in ionic radii and then deviations that can be traced to the LFSE. The general trend across the d block is the increase

<table>
<thead>
<tr>
<th>Molten CaO</th>
<th>CaO</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>2468</td>
<td>2936</td>
<td>2989</td>
</tr>
<tr>
<td>2600</td>
<td>2800</td>
<td>2843</td>
</tr>
<tr>
<td>2843</td>
<td>2800</td>
<td>2896</td>
</tr>
<tr>
<td>2904</td>
<td>2986</td>
<td>2936</td>
</tr>
<tr>
<td>2989</td>
<td>2989</td>
<td>2989</td>
</tr>
</tbody>
</table>

**Figure 20.7** The hydration enthalpy of M

2+ ions of the first row of the d block. The straight line shows the trend when the ligand-field stabilization energy has been subtracted from the observed values. Note the general trend to greater hydration enthalpy (more exothermic hydration) on crossing the period from left to right.
in lattice enthalpy from CaO (d⁰) to MnO (d⁵) as the ionic radii of the metals decrease (recall that lattice enthalpy is proportional to \(1/(r_+ + r_-)\), Section 3.12). The Ca²⁺ ion has an LFSE of zero as it has no d electrons and the Mn²⁺ ion, being high spin (O²⁻ is a weak field ligand), also has an LFSE of zero. For a linear increase in lattice enthalpy from calcium to manganese oxides we would expect the lattice enthalpies to increase by \((3810 – 3460)/5\) kJ mol⁻¹ from Ca²⁺ to Sc³⁺ to Ti⁴⁺ to V⁵⁺ to Mn⁶⁺. We would therefore expect TiO and VO to have lattice enthalpies of 3600 and 3670 kJ mol⁻¹, respectively. In fact, TiO (d⁲) has a lattice enthalpy of 3878 kJ mol⁻¹ and we can ascribe this difference of 278 kJ mol⁻¹ to an LFSE of \(0.8\Delta_O\). Likewise the actual lattice enthalpy of 3913 kJ mol⁻¹ for VO (d³) is 243 kJ mol⁻¹ greater than predicted, with this difference arising from an LFSE of \(1.2\Delta_O\).

Self-test 20.3 Account for the variation in lattice enthalpy of the solid fluorides in which each metal ion is surrounded by an octahedral array of F⁻ ions: MnF₂ (2780 kJ mol⁻¹), FeF₂ (2926 kJ mol⁻¹), CoF₂ (2976 kJ mol⁻¹), NiF₂ (3060 kJ mol⁻¹), and ZnF₂ (2985 kJ mol⁻¹).

(e) Tetrahedral complexes

Key points: In a tetrahedral complex, the e orbitals lie below the t₂g orbitals; only the high-spin case need be considered.

Four-coordinate tetrahedral complexes are second only in abundance to octahedral complexes for the 3d metals. The same kind of arguments based on crystal-field theory can be applied to these species as we used for octahedral complexes.

A tetrahedral crystal field splits d orbitals into two sets but with the two e orbitals (the \(d_x^2 - d_y^2\) and the \(d_z^2\)) lower in energy than the three t₂g orbitals (the \(d_{xy}\), the \(d_{xz}\), and the \(d_{yz}\)) (Fig. 20.8).¹ The fact that the e orbitals lie below the t₂g orbitals can be understood from a consideration of the spatial arrangement of the orbitals: the e orbitals point between the positions of the ligands and their partial negative charges whereas the t₂g orbitals point more directly towards the ligands (Fig. 20.9). A second difference is that the ligand-field splitting parameter in a tetrahedral complex, \(\Delta_T\), is less than \(\Delta_O\), as should be expected for complexes with fewer ligands, none of which is oriented directly at the d orbitals (in fact, \(\Delta_T = \frac{3}{5} \Delta_O\)). The pairing energy is invariably more unfavourable than \(\Delta_T\), and normally only high-spin tetrahedral complexes are encountered.

Ligand-field stabilization energies can be calculated in exactly the same way as for octahedral complexes. Since tetrahedral complexes are always high-spin, there is never any

¹ Because there is no centre of inversion in a tetrahedral complex, the orbital designation does not include the parity label g or u.
Values of ligand-field stabilization energies for tetrahedral complexes*

<table>
<thead>
<tr>
<th>Configuration</th>
<th>(N)</th>
<th>(\text{LFSE}/\Delta_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d^4)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(d^5)</td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>(d^6)</td>
<td>2</td>
<td>1.2</td>
</tr>
<tr>
<td>(d^7)</td>
<td>3</td>
<td>0.8</td>
</tr>
<tr>
<td>(d^8)</td>
<td>4</td>
<td>0.4</td>
</tr>
<tr>
<td>(d^9)</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>(d^{10})</td>
<td>6</td>
<td>4.6</td>
</tr>
</tbody>
</table>

*\(N\) is the number of unpaired electrons.

Table 20.5 Values of \(\Delta_s\) for representative tetrahedral complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\Delta_s/\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{VCl}_4)</td>
<td>9010</td>
</tr>
<tr>
<td>([\text{CoCl}_4]^{2-})</td>
<td>3300</td>
</tr>
<tr>
<td>([\text{CoBr}_4]^{2-})</td>
<td>2900</td>
</tr>
<tr>
<td>([\text{CoI}_4]^{2-})</td>
<td>2700</td>
</tr>
<tr>
<td>([\text{Co(NCS)}_4]^{2-})</td>
<td>4700</td>
</tr>
</tbody>
</table>

need to consider the pairing energy in the LFSE and the only differences compared with octahedral complexes are the order of occupation (e before \(t_l\)) and the contribution of each orbital to the total energy (\(\frac{2}{3}\Delta_{e}\) for an e orbital and \(-\frac{1}{3}\Delta_{t}\) for a \(t_l\) orbital). Table 20.4 lists the configurations of tetrahedral \(d^8\) complexes together with the calculated values of the LFSE and Table 20.5 lists some experimental values of \(\Delta_s\) for a number of complexes.

(f) Square-planar complexes

**Key point:** A \(d^8\) configuration, coupled with a strong ligand field, favours the formation of square-planar complexes. This tendency is enhanced with the 4d and 5d metals due to their larger size and the greater ease of electron pairing.

Although a tetrahedral arrangement of four ligands is the least sterically demanding arrangement, some complexes exist with four ligands in an apparently higher energy square-planar arrangement. A square-planar arrangement gives the \(d\)-orbital splitting shown in Fig. 20.10, with \(d_{xz}, d_{yz}\) raised above all the others. This arrangement may become energetically favourable when there are eight \(d\) electrons and the crystal field is strong enough to favour the low-spin \(d_{xy}\) configuration. In this configuration the electronic stabilization energy can more than compensate for any unfavourable steric interactions. Thus, many square-planar complexes are found for complexes of the large 4d- and 5d-series metals. By contrast, small 3d-series metal complexes such as \([\text{NiX}_4]^2-\), with \(X\) a halogen, are generally tetrahedral because the ligand-field splitting parameter is generally quite small and will not compensate sufficiently for the unfavourable steric interactions. Only when the ligand is high in the spectrochemical series is the LFSE large enough to result in the formation of a square-planar complex, as, for example, with \([\text{Ni(CN)}_4]^2-\). We have already noted that pairing energies for the 4d- and 5d-series metals tend to be lower than for the 3d-series metals, and this difference provides a further factor that favours the formation of low-spin square-planar complexes with these metals.

The sum of the three distinct orbital splittings in Fig. 20.10 is denoted \(\Delta_{sp}\). Simple theory predicts that \(\Delta_{sp} = 1.3\Delta_t\) for complexes of the same metal and ligands with the same \(M^-L\) bond lengths.

(g) Tetragonally distorted complexes: the Jahn–Teller effect

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

Six-coordinate \(d^9\) complexes of copper(II) usually depart considerably from octahedral geometry and show pronounced tetragonal distortions (Fig. 20.11). High-spin \(d^4\) (for instance,
Mn\textsuperscript{3+}) and low-spin d\textsuperscript{7} six-coordinate complexes (for instance, Ni\textsuperscript{3+}) may show a similar distortion, but they are less common. These distortions are manifestations of the **Jahn–Teller effect**: if the ground electronic configuration of a nonlinear complex is orbitally degenerate, and asymmetrically filled, then the complex distorts so as to remove the degeneracy and achieve a lower energy.

The physical origin of the effect is quite easy to identify. Thus, a tetragonal distortion of a regular octahedron, corresponding to extension along the z-axis and compression on the x- and y-axes, lowers the energy of the e\textsubscript{g}(d\textsubscript{z\textsuperscript{2}-r\textsuperscript{2}}) orbital and increases the energy of the e\textsubscript{g}(d\textsubscript{x\textsuperscript{2}-y\textsuperscript{2}}) orbital (Fig. 20.12). Therefore, if one or three electrons occupy the e\textsubscript{g} orbitals (as in high-spin d\textsuperscript{3}, low-spin d\textsuperscript{5}, and d\textsuperscript{9} complexes) a tetragonal distortion may be energetically advantageous. For example, in a d\textsuperscript{9} complex (with configuration that would be t\textsubscript{2g}\textsuperscript{3}e\textsubscript{g}\textsuperscript{6} in O\textsubscript{h}), such a distortion leaves two electrons in the d\textsubscript{z\textsuperscript{2}} orbital with a lower energy and one in the d\textsubscript{x\textsuperscript{2}-y\textsuperscript{2}} orbital with a higher energy. Similar distortions can occur with tetrahedral complexes.

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

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

A Jahn–Teller effect is possible for other electron configurations (for an octahedral complex the d\textsuperscript{3}, d\textsuperscript{5}, low-spin d\textsuperscript{7} and d\textsuperscript{9}, high-spin d\textsuperscript{5}, and d\textsuperscript{9} configurations, for a tetrahedral complex the d\textsuperscript{3}, d\textsuperscript{5}, d\textsuperscript{7}, d\textsuperscript{9}, and d\textsuperscript{11} configurations). However, as neither the t\textsubscript{2g} orbitals in an octahedral complex nor any of the d orbitals in a tetrahedral complex point directly at the ligands, the effect is too small to induce a measurable distortion in the structure.

### (h) Octahedral versus tetrahedral coordination

**Key points:** Consideration of the LFSE predicts that d\textsuperscript{3} and d\textsuperscript{5} ions strongly prefer an octahedral geometry over a tetrahedral one; for other configurations the preference is less pronounced, and LFSE has no bearing on the geometry of d\textsuperscript{3}, high-spin d\textsuperscript{5}, and d\textsuperscript{9} ions.

An octahedral complex has six M–L bonding interactions and, in the absence of significant steric and electronic effects, this arrangement will have a lower energy than a tetrahedral complex with just four M–L bonding interactions. We have already discussed the effects of steric bulk on a complex (Section 7.3), and have just seen the electronic reasons that favour a square-planar complex. We can now complete the discussion by considering the electronic effects that favour an octahedral complex over a tetrahedral one.

Figure 20.13 illustrates the variation of the LFSE for tetrahedral and high-spin octahedral complexes for all electronic configurations. It is apparent that, in terms of LFSE, octahedral geometries are strongly preferred over tetrahedral for d\textsuperscript{3} and d\textsuperscript{5} complexes: chromium(III) (d\textsuperscript{3}) and nickel(II) (d\textsuperscript{5}) do indeed show an exceptional preference for octahedral geometries. Similarly, d\textsuperscript{5} and d\textsuperscript{9} configurations show a preference for octahedral complexes (for example Mn(III) and Cu(II); note that the Jahn–Teller effect enhances this preference), whereas tetrahedral complexes of d\textsuperscript{3}, d\textsuperscript{5}, d\textsuperscript{7}, and d\textsuperscript{9} ions will not be too disfavoured; thus V(II) (d\textsuperscript{3}) and Co(II) (d\textsuperscript{9}) form tetrahedral complexes (MX\textsuperscript{2+}) with halide ligands. The geometry of complexes of ions with d\textsuperscript{3}, d\textsuperscript{5}, and d\textsuperscript{9} configurations will not be affected by the number of d electrons, as there is no LFSE for these species.

Because the size of the d-orbital splitting, and hence the LFSE, depends on the ligand, it follows that a preference for octahedral coordination will be least pronounced for weak-field ligands. With strong-field ligands, low-spin complexes might be preferred and, although the situation is complicated by the pairing energy, the LFSE of a low-spin octahedral complex will be greater than that of a high-spin complex. There will thus be a correspondingly greater preference for octahedral over tetrahedral coordination when the octahedral complex is low-spin.
This preference for octahedral over tetrahedral coordination plays an important role in the solid state by influencing the structures that are adopted by d-metal compounds. This influence is demonstrated by the ways in which the different metal ions A and B in spinels (of formula AB₂O₄, Sections 3.9b and 24.7c) occupy the octahedral or tetrahedral sites. Thus, Co₂O₄ is a normal spinel because the low-spin d⁴ Co(III) ion strongly favours octahedral coordination, resulting in (Co²⁺)(2Co³⁺)O₄; whereas FeO₂ (magnetite) is an inverse spinel because Fe(II), but not Fe(III), can acquire greater LFSE by occupying an octahedral site. Thus magnetite is formulated as (Fe²⁺)(Fe³⁺Fe³⁺)O₄.

(i) The Irving—Williams series

Key point: The Irving—Williams series summarizes the relative stabilities of complexes formed by M³⁺ ions, and reflects a combination of electrostatic effects and LFSE.

Figure 20.14 shows log Kᵣ values (Section 7.12) for complexes of the octahedral M³⁺ ions of the 3d series. The variation in formation constants shown there is summarized by the Irving—Williams series:

Ba³⁺ < Sr³⁺ < Ca²⁺ < Mg²⁺ < Mn³⁺ < Fe²⁺ < Co³⁺ < Ni²⁺ < Cu²⁺ > Zn²⁺

The order is relatively insensitive to the choice of ligands.

In general, the increase in stability correlates with ionic radius, which suggests that the Irving—Williams series reflects electrostatic effects. However, beyond Mn³⁺ there is a sharp increase in the value of Kᵣ for d⁴ Fe(II), d⁴ Co(II), d⁴ Ni(II), and d⁴ Cu(II), with strong-field ligands. These ions experience an additional stabilization proportional to the ligand-field stabilization energies (Table 20.2). There is one important exception: the stability of Cu(II) complexes is greater than that of Ni(II) even though Cu(II) has an additional antibonding σ electron. This anomaly is a consequence of the stabilizing influence of the Jahn–Teller effect, which results in strong binding of four of the ligands in the plane of the tetragonally distorted Cu(II) complex, and that stabilization enhances the value of Kᵣ.

20.2 Ligand-field theory

Crystal-field theory provides a simple conceptual model that can be used to interpret magnetic, spectroscopic, and thermochemical data by using empirical values of Δ₀. However, the theory is defective because it treats ligands as point charges or dipoles and does not take into account the overlap of ligand and metal atom orbitals. One consequence of this oversimplification is that crystal-field theory cannot account for the ligand spectrochemical series. Ligand-field theory, which is an application of molecular orbital theory that concentrates on the d orbitals of the central metal atom, provides a more substantial framework for understanding the origins of Δ₀.

The strategy for describing the molecular orbitals of a d-metal complex follows procedures similar to those described in Chapter 2 for bonding in polyatomic molecules: the valence orbitals on the metal and ligand are used to form symmetry-adapted linear combinations (SALCs; Section 6.6), and then estimating the relative energies of the molecular orbitals by using empirical energy and overlap considerations. These relative energies can be verified and positioned more precisely by comparison with experimental data (particularly UV/visible absorption and photoelectron spectroscopy).

We shall first consider octahedral complexes, initially taking into account only the metal–ligand σ bonding. We then consider the effect of π bonding, and see that it is essential for understanding Δ₀ (which is one reason why crystal-field theory cannot explain the spectrochemical series). Finally, we consider complexes with different symmetries, and see that similar arguments apply to them. Later in the chapter we shall see how information from optical spectroscopy is used to refine the discussion and provide quantitative data on the ligand-field splitting parameter and electron–electron repulsion energies.

(a) σ Bonding

Key point: In ligand-field theory, the building-up principle is used in conjunction with a molecular orbital energy level diagram constructed from metal atom orbitals and symmetry-adapted linear combinations of ligand orbitals.
We begin by considering an octahedral complex in which each ligand (L) has a single valence orbital directed towards the central metal atom (M); each of these orbitals has local \( \sigma \) symmetry with respect to the M–L axis. Examples of such ligands include the \( \text{NH}_3 \) molecule and the \( \text{F}^- \) ion.

In an octahedral \( (O_6) \) environment, the orbitals of the central metal atom divide by symmetry into four sets (Fig. 20.15 and Resource section 4):

<table>
<thead>
<tr>
<th>Metal orbital</th>
<th>Symmetry label</th>
<th>Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>( a_{1g} )</td>
<td>1</td>
</tr>
<tr>
<td>( p_x, p_y, p_z )</td>
<td>( t_{2g} )</td>
<td>3</td>
</tr>
<tr>
<td>( d_{x^2-y^2}, d_{xy} )</td>
<td>( e_g )</td>
<td>2</td>
</tr>
<tr>
<td>( d_{z^2}, d_{xz}, d_{yz} )</td>
<td>( t_{2g} )</td>
<td>3</td>
</tr>
</tbody>
</table>

Six symmetry-adapted linear combinations of the six ligand \( \sigma \) orbitals can also be formed. These combinations can be taken from Resource section 5 and are also shown in Fig. 20.15. One (unnormalized) SALC has symmetry \( a_{1g} \):

\[
\begin{align*}
a_{1g} &= \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6 \\
\end{align*}
\]

where \( \sigma_i \) denotes a \( \sigma \) orbital on ligand \( i \). There are three SALCs of symmetry \( t_{2u} \):

\[
\begin{align*}
t_{2u} &= \sigma_1 - \sigma_3, \quad \sigma_2 - \sigma_4, \quad \sigma_5 - \sigma_6 \\
\end{align*}
\]

and two SALCs of symmetry \( e_g \):

\[
\begin{align*}
e_g &= \sigma_1 - \sigma_2 + \sigma_3 - \sigma_4, \quad 2\sigma_2 + 2\sigma_3 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4 \\
\end{align*}
\]

These six SALCs account for all the ligand orbitals of \( \sigma \) symmetry: there is no combination of ligand \( \sigma \) orbitals that has the symmetry of the metal \( t_{2g} \) orbitals, so the latter do not participate in \( \sigma \) bonding.²

Molecular orbitals are formed by combining SALCs and metal atomic orbitals of the same symmetry. For example, the (unnormalized) form of an \( a_{1g} \) molecular orbital is \( c_M \psi_{M1} + c_L \psi_{L1a1g} \), where \( \psi_{M1} \) is the s orbital on the metal atom M and \( \psi_{L1a1g} \) is the ligand SALC of symmetry \( a_{1g} \). The metal s orbital and ligand \( a_{1g} \) SALC overlap to give two molecular orbitals, one bonding and one antibonding. Similarly, the doubly degenerate metal \( e_g \) orbitals and the ligand \( e_g \) SALCs overlap to give four molecular orbitals (two degenerate bonding, two degenerate antibonding), and the triply degenerate metal \( t_{2u} \) orbitals and the three \( t_{2u} \) SALCs overlap to give six molecular orbitals (three degenerate bonding, three degenerate antibonding). There are therefore six bonding combinations in all and six antibonding combinations. The three triply degenerate metal \( t_{2g} \) orbitals remain nonbonding and fully localized on the metal atom. Calculations of the resulting energies (adjusted to agree with a variety of spectroscopic data of the kind to be discussed in Section 20.4) result in the molecular orbital energy level diagram shown in Fig. 20.16.

The greatest contribution to the molecular orbital of lowest energy is from atomic orbitals of lowest energy (Section 2.9). For \( \text{NH}_3, \text{F}^- \), and most other ligands, the ligand \( \sigma \) orbitals are derived from atomic orbitals with energies that lie well below those of the metal d orbitals. As a result, the six bonding molecular orbitals of the complex are mainly ligand-orbital in character (that is, \( e_g^2 > c_M^2 \)). These six bonding orbitals can accommodate the 12 electrons provided by the six ligand lone pairs. The electrons that we can regard as provided by the ligands are therefore largely confined to the ligands in the complex, just as the crystal-field theory presumes. However, because the coefficients \( c_M \) are nonzero, the bonding molecular orbitals do have some d-orbital character and the ‘ligand electrons’ are partly delocalized on to the central metal atom.

The total number of electrons to accommodate, in addition to those supplied by the ligands, now depends on the number of d electrons, \( n \), supplied by the metal atom. These additional electrons enter the orbitals next in line for occupation, which are the nonbonding d orbitals (the \( t_{2g} \) orbitals) and the antibonding combination (the upper \( e_g \) orbitals) of the d orbitals and ligand orbitals. The \( t_{2g} \) orbitals are wholly confined (in the present approximation) to the metal atom and the antibonding \( e_g \) orbitals are largely metal atom in

²The normalization constants (with overlap neglected) are \( N(a_{1g}) = \frac{1}{\sqrt{6}}, N(t_{2u}) = \frac{1}{\sqrt{3}}, N(e_g) = \frac{1}{\sqrt{3}} \) for all three orbitals, and \( N(e_g) = \frac{1}{\sqrt{3}} \) and \( (\pi)^{\frac{1}{2}} \), respectively.
character too, so the \( n \) electrons supplied by the central atom remain largely on that atom. The frontier orbitals of the complex are therefore the nonbonding entirely metal \( t_{2g} \) orbitals and the antibonding, mainly metal \( e_g \) orbitals. Thus, we have arrived at an arrangement that is qualitatively the same as in crystal-field theory. In the ligand-field approach the octahedral ligand-field splitting parameter, \( \Delta_{o} \), is the separation between the molecular orbitals largely, but not completely, confined to the metal atom, Fig. 20.16.

With the molecular orbital energy level diagram established, we use the building-up principle to construct the ground-state electron configuration of the complex. For a \( d^n \) complex, there are \( 12 + n \) electrons to accommodate. The six bonding molecular orbitals accommodate the 12 electrons supplied by the ligands. The remaining \( n \) electrons are accommodated in the nonbonding \( t_{2g} \) orbitals and the antibonding \( e_g \) orbitals. Now the story is essentially the same as for crystal-field theory, the types of complexes that are obtained (high-spin or low-spin, for instance) depending on the relative values of \( \Delta_{o} \) and the pairing energy \( P \). The principal difference from the crystal-field discussion is that ligand-field theory gives deeper insight into the origin of the ligand-field splitting, and we can begin to understand why some ligands are strong and others are weak. For instance, a good \( \sigma \)-donor ligand should result in strong metal–ligand overlap, hence a more strongly antibonding \( e_g \) set and consequently a larger value of \( \Delta_{o} \). However, before drawing further conclusions, we must go on to consider what crystal-field theory ignores completely, the role of \( \pi \) bonding.
The photoelectron spectrum of gas-phase [Mo(CO)]$_6$ is shown in Fig. 20.17. Use the spectrum to infer the energies of the molecular orbitals of the complex.

**Answer** We need to identify the electron configuration of the complex, and then match the order of ionization energies to the order of the orbitals from which the electrons are likely to come. Twelve electrons are provided by the six CO ligands (treated as :CO); they enter the bonding orbitals and result in the configuration $\pi^6 \sigma^6$. The oxidation number of molybdenum, Group 6, is 0, so Mo provides a further six valence electrons. The ligand and metal valence electrons are distributed over the orbitals shown in the box in Fig. 20.15 and, as CO is a strong-field ligand, the ground-state electron configuration of the complex is expected to be low-spin $\pi^6 \sigma^6$. The HOMOs are the three $t_{2g}$ orbitals largely confined to the Mo atom, and their energy can be identified by ascribing the peak of lowest ionization energy (close to 8 eV) to them. The group of ionization energies around 14 eV are probably due to the Mo–CO $\sigma$-bonding orbitals. The value of 14 eV is close to the ionization energy of CO itself, so the variety of peaks at that energy also arise from bonding orbitals in CO.

**Selftest 20.4** Suggest an interpretation of the photoelectron spectra of [Fe(C,H$_5$)$_2$] and [Mg(C$_5$H$_7$)$_2$] shown in Fig. 20.18.

(b) $\pi$ Bonding

**Key points:** $\pi$-Donor ligands decrease $\Delta\nu$ whereas $\pi$-acceptor ligands increase $\Delta\nu$; the spectrochemical series is largely a consequence of the effects of $\pi$ bonding when such bonding is feasible.

If the ligands in a complex have orbitals with local $\pi$ symmetry with respect to the M–L axis (as two of the p orbitals of a halide ligand have), they may form bonding and antibonding $\pi$ orbitals with the metal orbitals (Fig. 20.19). For an octahedral complex the combinations that can be formed from the ligand $\pi$ orbitals include SALCs of $t_{2g}$ symmetry. These ligand combinations have not overlap with the metal $t_{2g}$ orbitals, which are therefore no longer purely nonbonding on the metal atom. Depending on the relative energies of the ligand and metal orbitals, the energies of the now molecular $t_{2g}$ orbitals lie above or below the energies they had as nonbonding atomic orbitals, so $\Delta\nu$ is decreased or increased, respectively.

To explore the role of $\pi$ bonding in more detail, we need two of the general principles described in Chapter 2. First, we shall make use of the idea that, when atomic orbitals overlap strongly, they mix strongly; the resulting bonding molecular orbitals are significantly lower in energy and the antibonding molecular orbitals are significantly higher in energy than the atomic orbitals. Second, we note that atomic orbitals with similar energies interact strongly, whereas those of very different energies mix only slightly even if their overlap is large.

A $\pi$-donor ligand is a ligand that, before any bonding is considered, has filled orbitals of $\pi$ symmetry around the M–L axis. Such ligands include Cl$^-$, Br$^-$, OH$^-$, O$_2^-$ and even H$_2$O. In Lewis acid–base terminology (Section 4.9), a $\pi$-donor ligand is a $\pi$ base. The energies of the full $\pi$ orbitals on the ligands will not normally be higher than their $\sigma$-donor orbitals (HOMO) and must therefore also be lower in energy than the metal d orbitals. Because the full $\pi$ orbitals of $\pi$ donor ligands lie lower in energy than the partially filled d orbitals of the metal, when they form molecular orbitals with the metal $t_{2g}$ orbitals, the antibonding combination lies lower than the ligand orbitals and the antibonding combination lies above the energy of the d orbitals of the free metal atom (Fig. 20.20). The electrons supplied by the ligand $\pi$ orbitals occupy and fill the bonding combinations, leaving the electrons originally in the d orbitals of the central metal atom to occupy the antibonding $t_{2g}$ orbitals. The net effect is that the previously nonbonding metal $t_{2g}$ orbitals become antibonding and hence are raised closer in energy to the antibonding $e_g$ orbitals. It follows that $\pi$-donor ligands decrease $\Delta\nu$.

A $\pi$-acceptor ligand is a ligand that has empty $\pi$ orbitals that are available for occupation. In Lewis acid–base terminology, a $\pi$-acceptor ligand is a $\pi$ acid. Typically, the $\pi$-acceptor orbitals are vacant antibonding orbitals on the ligand (usually the LUMO), as in CO and N$_2$, which are higher in energy than the metal d orbitals. The two $\pi^*$ orbitals of CO, for instance, have their largest amplitude on the C atom and have the correct symmetry for overlap with the metal $t_{2g}$ orbitals, so CO can act as a $\pi$-acceptor ligand.

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**Figure 20.17** The He(Il) (30.4 nm) photoelectron spectrum of Mo(CO)$_6$. With six electrons from Mo and twelve from CO, the ground-state configuration of the complex is $\pi^6 \sigma^6$. (From B.R. Higginson, D.R. Lloyd, P. Burroughs, D.M. Gibson, and A.F. Orchard, J. Chem. Soc., Faraday II, 1973, 69, 1659.)

**Figure 20.18** Photoelectron spectra of ferrocene and magnesocene.

**Figure 20.19** The $\pi$ overlap that may occur between a ligand $p$ orbital perpendicular to the M–L axis and a metal $d_y$ orbital.

**Figure 20.20** Using a photoelectron spectrum to obtain information about a complex

The photoelectron spectrum of gas-phase [Mo(CO)$_6$] is shown in Fig. 20.17. Use the spectrum to infer the energies of the molecular orbitals of the complex.

**Answer** We need to identify the electron configuration of the complex, and then match the order of ionization energies to the order of the orbitals from which the electrons are likely to come. Twelve electrons are provided by the six CO ligands (treated as :CO); they enter the bonding orbitals and result in the configuration $\pi^6 \sigma^6$. The oxidation number of molybdenum, Group 6, is 0, so Mo provides a further six valence electrons. The ligand and metal valence electrons are distributed over the orbitals shown in the box in Fig. 20.15 and, as CO is a strong-field ligand, the ground-state electron configuration of the complex is expected to be low-spin $\pi^6 \sigma^6$. The HOMOs are the three $t_{2g}$ orbitals largely confined to the Mo atom, and their energy can be identified by ascribing the peak of lowest ionization energy (close to 8 eV) to them. The group of ionization energies around 14 eV are probably due to the Mo–CO $\sigma$-bonding orbitals. The value of 14 eV is close to the ionization energy of CO itself, so the variety of peaks at that energy also arise from bonding orbitals in CO.

**Selftest 20.4** Suggest an interpretation of the photoelectron spectra of [Fe(C,H$_5$)$_2$] and [Mg(C$_5$H$_7$)$_2$] shown in Fig. 20.18.

(b) $\pi$ Bonding

**Key points:** $\pi$-Donor ligands decrease $\Delta\nu$ whereas $\pi$-acceptor ligands increase $\Delta\nu$; the spectrochemical series is largely a consequence of the effects of $\pi$ bonding when such bonding is feasible.

If the ligands in a complex have orbitals with local $\pi$ symmetry with respect to the M–L axis (as two of the p orbitals of a halide ligand have), they may form bonding and antibonding $\pi$ orbitals with the metal orbitals (Fig. 20.19). For an octahedral complex the combinations that can be formed from the ligand $\pi$ orbitals include SALCs of $t_{2g}$ symmetry. These ligand combinations have not overlap with the metal $t_{2g}$ orbitals, which are therefore no longer purely nonbonding on the metal atom. Depending on the relative energies of the ligand and metal orbitals, the energies of the now molecular $t_{2g}$ orbitals lie above or below the energies they had as nonbonding atomic orbitals, so $\Delta\nu$ is decreased or increased, respectively.

To explore the role of $\pi$ bonding in more detail, we need two of the general principles described in Chapter 2. First, we shall make use of the idea that, when atomic orbitals overlap strongly, they mix strongly; the resulting bonding molecular orbitals are significantly lower in energy and the antibonding molecular orbitals are significantly higher in energy than the atomic orbitals. Second, we note that atomic orbitals with similar energies interact strongly, whereas those of very different energies mix only slightly even if their overlap is large.

A $\pi$-donor ligand is a ligand that, before any bonding is considered, has filled orbitals of $\pi$ symmetry around the M–L axis. Such ligands include Cl$^-$, Br$^-$, OH$^-$, O$_2^-$ and even H$_2$O. In Lewis acid–base terminology (Section 4.9), a $\pi$-donor ligand is a $\pi$ base. The energies of the full $\pi$ orbitals on the ligands will not normally be higher than their $\sigma$-donor orbitals (HOMO) and must therefore also be lower in energy than the metal d orbitals. Because the full $\pi$ orbitals of $\pi$ donor ligands lie lower in energy than the partially filled d orbitals of the metal, when they form molecular orbitals with the metal $t_{2g}$ orbitals, the antibonding combination lies lower than the ligand orbitals and the antibonding combination lies above the energy of the d orbitals of the free metal atom (Fig. 20.20). The electrons supplied by the ligand $\pi$ orbitals occupy and fill the bonding combinations, leaving the electrons originally in the d orbitals of the central metal atom to occupy the antibonding $t_{2g}$ orbitals. The net effect is that the previously nonbonding metal $t_{2g}$ orbitals become antibonding and hence are raised closer in energy to the antibonding $e_g$ orbitals. It follows that $\pi$-donor ligands decrease $\Delta\nu$.

A $\pi$-acceptor ligand is a ligand that has empty $\pi$ orbitals that are available for occupation. In Lewis acid–base terminology, a $\pi$-acceptor ligand is a $\pi$ acid. Typically, the $\pi$-acceptor orbitals are vacant antibonding orbitals on the ligand (usually the LUMO), as in CO and N$_2$, which are higher in energy than the metal d orbitals. The two $\pi^*$ orbitals of CO, for instance, have their largest amplitude on the C atom and have the correct symmetry for overlap with the metal $t_{2g}$ orbitals, so CO can act as a $\pi$-acceptor ligand.
Phosphines (PR₃) are also able to accept π-electron density and also act as π acceptors (Section 22.6).

Because the π-acceptor orbitals on most ligands are higher in energy than the metal d orbitals, they form molecular orbitals in which the bonding t₂g combinations are largely of metal d-orbital character (Fig. 20.21). These bonding combinations lie lower in energy than the d orbitals themselves. The net result is that π-acceptors increase Δ₀.

We can now put the role of π bonding in perspective. The order of ligands in the spectrochemical series is partly that of the strengths with which they can participate in M—L σ bonding. For example, both CH₃ and H are very high in the spectrochemical series because they are very strong σ donors. However, when π bonding is significant, it has a strong influence on Δ₀: π-donor ligands decrease Δ₀, and π-acceptor ligands increase Δ₀. This effect is responsible for CO (a strong π acceptor) being high on the spectrochemical series and for OH⁻ (a strong π donor) being low in the series. The overall order of the spectrochemical series may be interpreted in broad terms as dominated by π effects (with a few important exceptions), and in general the series can be interpreted as follows:

\[-\text{increasing } \Delta_0 \rightarrow \text{π donor } < \text{ weak π donor } < \text{ no π effects } < \text{ π acceptor}\]

Representative ligands that match these classes are

<table>
<thead>
<tr>
<th></th>
<th>π donor</th>
<th>weak π donor</th>
<th>no π effects</th>
<th>π acceptor</th>
</tr>
</thead>
<tbody>
<tr>
<td>I⁻, Br⁻, Cl⁻, F⁻</td>
<td>H₂O</td>
<td>NH₃</td>
<td>PR₃, CO</td>
<td></td>
</tr>
</tbody>
</table>

Notable examples of where the effect of σ bonding dominates include amines (NR₃), CH₃, and H, none of which has orbitals of π symmetry of an appropriate energy and thus are neither π-donor nor π-acceptor ligands. It is important to note that the classification of a ligand as strong-field or weak-field does not give any guide as to the strength of the M—L bond.

**Electronic spectra**

Now that we have considered the electronic structure of d-metal complexes, we are in a position to understand their electronic spectra and to use the data they provide to refine the discussion of structure. The magnitudes of ligand-field splittings are such that the energy of electronic transitions corresponds to an absorption of ultraviolet radiation and visible light. However, the presence of electron–electron repulsions within the metal orbitals means that the absorption frequencies are not in general a direct portrayal of the ligand-field splitting. The role of electron–electron repulsions was originally determined by the analysis of atoms and ions in the gas phase, and much of that information can be used in the analysis of the spectra of metal complexes provided we take into account the lower symmetry of a complex.

Keep in mind that the purpose of the following development is to find a way to extract the value of the ligand-field splitting parameter from the electronic absorption spectrum of a complex with more than one d electron, when electron–electron repulsions are important. First, we discuss the spectra of free atoms and see how to take electron–electron repulsions into account. Then we see what energy states atoms adopt when they are embedded in an octahedral ligand field. Finally, we see how to represent the energies of these states for various field strengths and electron–electron repulsion energies (in the Tanabe–Sugano diagrams of Section 20.4e), and how to use these diagrams to extract the value of the ligand-field splitting parameter.

**20.3 Electronic spectra of atoms**

**Key point:** Electron–electron repulsions result in multiple absorptions in the electronic spectrum.

Figure 20.22 sets the stage for our discussion by showing the electronic absorption spectrum of the d⁶ complex [Cr(NH₃)₆]³⁺ in aqueous solution. The band at lowest energy (longest wavelength) is very weak; later we shall see that it is an example of a ‘spin-forbidden’ transition. Next are two bands with intermediate intensities; these are ‘spin-allowed’ transitions between the t₂g and e_g orbitals of the complex, which are mainly derived from the...
metal d orbitals. The third feature in the spectrum is an intense charge-transfer band at short wavelength (labelled CT, denoting 'charge transfer'), of which only the low-energy tail is evident in the illustration.

One problem that immediately confronts us is why two absorptions can be ascribed to the apparently single transition $t_2^1 e^1 \leftarrow t_2^3$. This splitting of a single transition into two bands is in fact an outcome of the electron-electron repulsions mentioned above. To understand how it arises, and to extract the information it contains, we need to consider the spectra of free atoms and ions.

(a) Spectroscopic terms

Key points: Different microstates exist for the same electronic configuration; for light atoms, Russell–Saunders coupling is used to describe the terms, which are specified by symbols in which the value of $L$ is indicated by one of the letters $S, P, D, ...$, and the value of $2S + 1$ is given as a left superscript.

In Chapter 1 we expressed the electronic structures of atoms by giving their electronic configurations, the designation of the number of electrons in each orbital (as in 1s$^2$2s$^1$ for Li). However, a configuration is an incomplete description of the arrangement of electrons in atoms. In the configuration 2p$^2$, for instance, the two electrons might occupy orbitals with different orientations of their orbital angular momenta (that is, with different values of $m_l$ from among the possibilities $+1, 0, -1$ that are available when $l = 1$). Similarly, the designation 2p$^2$ tells us nothing about the spin orientations of the two electrons $m_s$ but does indicate the relative orientation of the spins of the electrons. The atom may in fact have several different states of total orbital and spin angular momenta, each one corresponding to the occupation of orbitals with different values of $m_l$ by electrons with different values of $m_s$. The different ways in which the electrons can occupy the orbitals specified in the configuration are called the microstates of the configuration. For example, one microstate of a 2p$^2$ configuration is $(1^+, 1^-)$; this notation signifies that both electrons occupy an orbital with $m_l = +1$ but do so with opposite spins, the superscript + indicating $m_s = +\frac{1}{2}$ and − indicating $m_s = -\frac{1}{2}$. Another microstate of the same configuration is $(1^-, 0^-)$. In this microstate, both electrons have $m_s = +\frac{1}{2}$ but one occupies the 2p orbital with $m_l = -1$ and the other occupies the orbital with $m_l = 0$.

The microstates of a given configuration have the same energy only if electron–electron repulsions on the atom are negligible. However, because atoms and most molecules are compact, interelectronic repulsions are strong and cannot always be ignored. As a result, microstates that correspond to different relative spatial distributions of electrons have different energies. If we group together the microstates that have the same energy when electron–electron repulsions are taken into account, we obtain the spectroscopically distinguishable energy levels called terms.

For light atoms and the 3d series, it turns out that the most important property of a microstate for helping us to decide its energy is the relative orientation of the spins of the electrons.

Figure 20.22 The spectrum of the d$^3$ complex [Cr(NH$_3$)$_6$]$^{3+}$, which illustrates the features studied in this section, and the assignments of the transitions as explained in the text.
Next in importance is the relative orientation of the orbital angular momenta of the electrons. It follows that we can identify the terms of light atoms and put them in order of energy by sorting the microstates according to their total spin quantum number $S$ (which is determined by the relative orientation of the individual spins) and then according to their total orbital angular momentum quantum number $L$ (which is determined by the relative orientation of the individual angular momenta of the electrons). For heavy atoms, such as those of the 4d and 5d series, the relative orientations of orbital momenta or of spin momenta are less important. In these atoms the spin and orbital angular momenta of individual electrons are strongly coupled together by spin–orbit coupling, so the relative orientation of the spin and orbital angular momenta of each electron is the most important feature for determining the energy. The terms of heavy atoms are therefore sorted on the basis of the values of the total angular momentum quantum number $j$ for an electron in each microstate.

The process of combining electron angular momenta by summing first the spins, then the orbital momenta, and finally combining the two resultants is called Russell–Saunders coupling. This coupling scheme is used to identify the terms of light atoms (i.e. the 3d metals), and we consider it in detail here. The coupling scheme most appropriate to heavy atoms (that is, atoms of the 4d and 5d series of elements) is called jj-coupling, but we shall not consider it further.

Our first task is to identify the values of $L$ and $S$ that can arise from the orbital and spin angular momenta of individual electrons. Suppose we have two electrons with quantum numbers $l_1, s_1$ and $l_2, s_2$. Then, according to the Clebsch–Gordan series, the possible values of $L$ and $S$ are

\[ L = l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2| \quad S = s_1 + s_2, s_1 + s_2 - 1, \ldots, |s_1 - s_2| \]  

(20.3)

(The modulus signs appear because neither $L$ nor $S$ can, by definition, be negative.) For example, an atom with configuration $d_1 l_2$ (i.e. $l_1 = 2, l_2 = 2$) can have the following values of $L$:

\[ L = 2 + 2, 2 + 2 - 1, \ldots, |2 - 2| = 4, 3, 2, 1, 0 \]

The total spin (because $s_1 = \frac{1}{2}, s_2 = \frac{1}{2}$) can be

\[ S = \frac{1}{2} + \frac{1}{2}, \frac{1}{2} + \frac{1}{2} - 1, \ldots, |\frac{1}{2} - \frac{1}{2}| = 1, 0 \]

To find the values of $L$ and $S$ for atoms with three electrons, we continue the process by combining $l_1$ with the value of $L$ just obtained, and likewise for $s_1$.

Once $L$ and $S$ have been found, we can write down the allowed values of the quantum numbers $M_L$ and $M_S$:

\[ M_L = L, L - 1, \ldots, -L \quad M_S = S, S - 1, \ldots, -S \]

These quantum numbers give the orientation of the angular momentum relative to an arbitrary axis: there are $2L + 1$ values of $M_L$ for a given value of $L$ and $2S + 1$ values of $M_S$ for a given value of $S$. The values of $M_L$ and $M_S$ for a given microstate can be found very easily by adding together the values of $m_L$ or $m_S$ for the individual electrons. Therefore, if one electron has the quantum number $m_{l_1}$ and the other has $m_{l_2}$, then

\[ M_L = m_{l_1} + m_{l_2} \]

A similar expression applies to the total spin:

\[ M_S = m_{s_1} + m_{s_2} \]

Thus, for example, $(0^-, -1^-)$ is a microstate with $M_L = 0 - 1 = -1$ and $M_S = \frac{1}{2} + (-\frac{1}{2}) = 0$ and may contribute to any term for which these two quantum numbers apply.

By analogy with the notation $s, p, d, \ldots$ for orbitals with $l = 0, 1, 2, \ldots$, the total orbital angular momentum of an atomic term is denoted by the equivalent uppercase letter:

\[ L = 0 \quad 1 \quad 2 \quad 3 \quad 4 \]

\[ S = 0 \quad \frac{1}{2} \quad 1 \quad \frac{3}{2} \quad 2 \]

\[ 2S + 1 = 1 \quad 2 \quad 3 \quad 4 \quad 5 \]

The total spin is normally reported as the value of $2S + 1$, which is called the multiplicity of the term.
The multiplicity is written as a left superscript on the letter representing the value of \( L \), and the entire label of a term is called a term symbol. Thus, the term symbol \( ^3P \) denotes a term (a collection of nearly degenerate states) with \( L = 1 \) and \( S = 1 \), and is called a triplet term.

**EXAMPLE 20.5** Deriving term symbols

Give the term symbols for an atom with the configuration (a) \( s^1 \), (b) \( p^1 \), and (c) \( s^1 p^1 \).

**Answer** We need to use the Clebsch–Gordan series to couple any angular momenta, identify the letter for the term symbol from the table above, and then attach the multiplicity as a left superscript. (a) The single s electron has \( l = 0 \) and \( s = \frac{1}{2} \). Because there is only one electron, \( L = 0 \) (an S term), \( S = s = \frac{1}{2} \), and \( 2S + 1 = 2 \) (a doublet term). The term symbol is therefore \( ^2S \). (b) For a single p electron, \( l = 1 \) so \( L = 1 \) and the term is \( ^3P \). (These terms arise in the spectrum of an alkali metal atom, such as Na.) (c) With one s and one p electron, \( L = 0 + 1 = 1 \), a P term. The electrons may be paired (\( S = 0 \)) or parallel (\( S = 1 \)). Hence both \( ^1P \) and \( ^3P \) terms are possible.

**Selftest 20.5** What terms arise from a \( p^1d^1 \) configuration?

(b) The classification of microstates

**Key point:** The allowed terms of a configuration are found by identifying the values of \( L \) and \( S \) to which the microstates of an atom can contribute.

The Pauli principle restricts the microstates that can occur in a configuration and consequently affects the terms that can occur. For example, two electrons cannot both have the same spin and be in a d orbital with \( m_l = +2 \). Therefore, the microstate \( (2^+,2^-) \) is forbidden and so are the values of \( L \) and \( S \) to which such a microstate might contribute. We shall illustrate how to determine what terms are allowed by considering a \( d^2 \) configuration, as the outcome will be useful in the discussion of the complexes encountered later in the chapter. An example of a species with a \( d^2 \) configuration is a Ti\(^{2+}\) ion.

We start the analysis by setting up a table of microstates of the \( d^2 \) configuration (Table 20.6); only the microstates allowed by the Pauli principle have been included. We then use a process of elimination to classify all the microstates. First, we note the largest value of \( M_s \), which for a \( d^2 \) configuration is +4. This state must belong to a term with \( L = 4 \) (a G term). Table 20.6 shows that the only value of \( M_s \) that occurs for this term is \( M_s = 0 \), so the G term must be a singlet. Moreover, as there are nine values of \( M_s \) when \( L = 4 \), one of the microstates in each of the boxes in the column below \( (2^+,2^-) \) must belong to this term.\(^3\) We can therefore strike out one microstate from each row in the central column of Table 20.6, which leaves 36 microstates.

<table>
<thead>
<tr>
<th>( M_s )</th>
<th>( -1 )</th>
<th>( M_s )</th>
<th>( 0 )</th>
<th>( +1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>+4</td>
<td>( 2^+,2^- )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+3</td>
<td>( 2^+,1^- )</td>
<td>( 2^+,1^- )</td>
<td>( 2^+,1^- )</td>
<td></td>
</tr>
<tr>
<td>+2</td>
<td>( 2^+,0^+ )</td>
<td>( 2^+,0^+ )</td>
<td>( 2^+,0^+ )</td>
<td></td>
</tr>
<tr>
<td>+1</td>
<td>( 2^+,1^- )</td>
<td>( 2^+,1^- )</td>
<td>( 2^+,1^- )</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>( 1^-,1^- )</td>
<td>( 1^-,1^- )</td>
<td>( 1^-,1^- )</td>
<td></td>
</tr>
<tr>
<td>−1 to −4*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^3\)In fact, it is unlikely that one of the microstates itself will correspond to one of these states: in general, a state is a linear combination of microstates. However, as \( N \) linear combinations can be formed from \( N \) microstates, each time we cross off one microstate, we are taking one linear combination into account, so the bookkeeping is correct even though the detail may be wrong.

Table 20.6 Microstates of the \( d^2 \) configuration
The next largest value is $M_z = +3$, which must stem from $L = 3$ and hence belong to an $F$ term. That row contains one microstate in each column (that is, each box contains one unassigned combination for $M_z = -1, 0, +1$), which signifies $S = 1$ and therefore a triplet term. Hence the microstates belong to $^3F$. The same is true for one microstate in each of the rows down to $M_z = -3$, which accounts for a further $3 \times 7 = 21$ microstates. If we strike out one state in each of the 21 boxes, we are left with 15 to be assigned.

There is one unassigned microstate in the row with $M_z = +2$ (which must arise from $L = 2$) and the column under $M_z = 0$ ($S = 0$), which must therefore belong to a $^3D$ term. This term has five values of $M_z$, which removes one microstate from each row in the column headed $M_z = 0$ down to $M_z = -2$, leaving 10 microstates unassigned. Because these unassigned microstates include one with $M_z = +1$ and $M_z = +1$, nine of these microstates must belong to a $^3P$ term. There now remains only one microstate in the central box of the table, with $M_z = 0$ and $M_z = 0$. This microstate must be the one and only state of a $^1S$ term (which has $L = 0$ and $S = 0$).

At this point we can conclude that the terms of a $3d^2$ configuration are $^1G$, $^3F$, $^3D$, $^3P$, and $^1S$. These terms account for all 45 permitted states (see table in the margin).

### (c) The energies of the terms

**Key point:** Hund’s rules indicate the likely ground term of a gas-phase atom or ion.

Once the values of $L$ and $S$ that can arise from a given configuration are known, it is possible to identify the term of lowest energy by using Hund’s rules. The first of these empirical rules was introduced in Section 1.7, where it was expressed as ‘the lowest energy configuration is achieved if the electron spins are parallel’. Because a high value of $S$ stems from parallel electron spins, an alternative statement is

1. For a given configuration, the term with the greatest multiplicity lies lowest in energy.

The rule implies that a triplet term of a configuration (if one is permitted) has a lower energy than a singlet term of the same configuration. For the $d^2$ configuration, this rule predicts that the ground state will be either $^3F$ or $^3P$.

By inspecting spectroscopic data, Hund also identified a second rule for the relative energies of the terms of a given multiplicity:

2. For a term of given multiplicity, the term with the greatest value of $L$ lies lowest in energy.

The physical justification for this rule is that when $L$ is high, the electrons can stay clear of one another and hence experience a lower repulsion. If $L$ is low, the electrons are more likely to be closer to each other, and hence repel one another more strongly. The second rule implies that, of the two triplet terms of a $d^2$ configuration, the $^3F$ term is lower in energy than the $^3P$ term. It follows that the ground term of a $d^2$ species such as Ti$^{2+}$ is expected to be $^3F$.

The spin multiplicity rule is fairly reliable for predicting the ordering of terms, but the ‘greatest $L$’ rule is reliable only for predicting the ground term, the term of lowest energy; there is generally little correlation of $L$ with the order of the higher terms. Thus, for $d^2$ the rules predict the order

$$^3F < ^3P < ^1G < ^3D < ^1S$$

but the order observed for Ti$^{2+}$ from spectroscopy is

$$^3F < ^3D < ^3P < ^1G < ^1S$$

Normally, all we want to know is the identity of the ground term of an atom or ion. The procedure may then be simplified and summarized as follows:

1. Identify the microstate that has the highest value of $M_z$.
   This step tells us the highest multiplicity of the configuration.

2. Identify the highest permitted value of $M_z$ for that multiplicity.
   This step tells us the highest value of $L$ consistent with the highest multiplicity.
**Example 20.6 Identifying the ground term of a configuration**

What is the ground term of the configurations (a) \(3d^6\) of Mn\(^{2+}\) and (b) \(3d^5\) of Cr\(^{3+}\)?

**Answer** First we need to identify the term with maximum multiplicity, as this will be the ground term. Then we need to identify the \(L\) value for any terms that have the maximum multiplicity, for the term with the highest \(L\) value will be the ground term. (a) Because the \(d^6\) configuration permits occupation of each \(d\) orbital singly with parallel spins, the maximum value of \(S\) is \(\frac{1}{2}\), giving a multiplicity of \(2 \times \frac{1}{2} + 1 = 6\), a sextet term. If each of the electrons is to have the same spin quantum number, all must occupy different orbitals and hence have different \(M_l\) values. Thus, the \(M_l\) values of the occupied orbitals will be \(+2\), \(+1\), \(0\), \(-1\), and \(-2\). This configuration is the only one possible for a sextet term. Because the sum of the \(M_l\) is 0, it follows that \(L = 0\) and the term is \(^3S\). (b) For the configuration \(d^5\), the maximum multiplicity corresponds to all three electrons having the same spin quantum number, so \(S = \frac{3}{2}\). The multiplicity is therefore \(2 \times \frac{3}{2} + 1 = 4\), a quartet. Again, the three \(M_l\) values must be different if the electrons are all parallel. There are several possible arrangements that give quartet terms, but the one that gives a maximum value of \(M_l\) has the three electrons with \(M_l = +2\), \(+1\), and \(0\), giving a total of +3, which must arise from a term with \(L = 3\), an \(^4F\) term. Hence, the ground term of \(d^5\) is \(^4F\).

**Self-test 20.6** Identify the ground terms of (a) \(2p^2\) and (b) \(3d^1\). (Hint: Because \(d^1\) is one electron short of a closed shell with \(L = 0\) and \(S = 0\), treat it on the same footing as a \(d^1\) configuration.)

Figure 20.23 shows the relative energies of the terms for the \(d^1\) and \(d^3\) configurations of free atoms. Later, we shall see how to extend these diagrams to include the effect of a crystal field (Section 20.4).

**(d) Racah parameters**

**Key points:** The Racah parameters summarize the effects of electron–electron repulsion on the energies of the terms that arise from a single configuration; the parameters are the quantitative expression of the ideas underlying Hund’s rules and account for deviations from them.

Different terms of a configuration have different energies on account of the repulsion between electrons. To calculate the energies of the terms we must evaluate these electron–electron repulsion energies as complicated integrals over the orbitals occupied by the electrons. Mercifully, however, all the integrals for a given configuration can be collected together in three specific combinations and the repulsion energy of any term of a configuration can be expressed as a sum of these three quantities. The three combinations of integrals are called the **Racah parameters** and denoted \(A\), \(B\), and \(C\). The parameter \(A\) corresponds to an average of the total interelectron repulsion, and \(B\) and \(C\) relate to the repulsion energies between individual \(d\) electrons. We do not even need to know the theoretical values of the parameters or the theoretical expressions for them because it is more reliable to use \(A\), \(B\), and \(C\) as empirical quantities obtained from gas-phase atomic spectroscopy.

Each term stemming from a given configuration has an energy that may be expressed as a linear combination of all three Racah parameters. For a \(d^2\) configuration a detailed analysis shows that

\[
E(^1S) = A + 14B + 7C \quad E(^1G) = A + 4B + 2C \quad E(^1D) = A - 3B + 2C
\]

\[
E(^3P) = A + 7B \quad E(^3F) = A - 8B
\]

The values of \(A\), \(B\), and \(C\) can be determined by fitting these expressions to the observed energies of the terms. Note that \(A\) is common to all the terms (as remarked above it is the average of the total interelectron repulsion energy); therefore, if we are interested only in their relative energies, we do not need to know its value. All three Racah parameters are positive as they represent electron–electron repulsions. Therefore, provided \(C > 5B\), the energies of the terms of the \(d^2\) configuration lie in the order

\[^3F < ^3P < ^1D < ^1G < ^1S\]

This order is nearly the same as obtained by using Hund’s rules. However, if \(C < 5B\), the advantage of having an occupation of orbitals that corresponds to a high orbital angular momentum is greater than the advantage of having a high multiplicity, and the \(^3P\) term lies above \(^1D\) (as is in fact the case for Ti\(^{2+}\)). Table 20.7 shows some experimental values of
Electronic spectra of complexes

The preceding discussion related only to free atoms, and we will now expand our discussion to encompass complex ions. The spectrum of $[\text{Cr(NH}_3)_6]^3-$ in Fig. 20.22 has two central bands with intermediate intensities and with energies that differ on account of the electron-electron repulsions (as we explain soon). Because both the transitions are between orbitals that are predominantly metal d orbital in character, with a separation characterized by the strength of the ligand-field splitting parameter $\Delta_{\text{t}_{2g}}$, these two transitions are called $\text{d} \leftarrow \text{d}$ transitions or ligand-field transitions.

(a) Ligand-field transitions

**Key point:** Electron–electron repulsion splits ligand-field transitions into components with different energies.

According to the discussion in Section 20.1, we expect the octahedral $d^3$ complex $[\text{Cr(NH}_3)_6]^3-$ to have the ground-state configuration $t_{2g}^3$. The absorption near 25 000 cm$^{-1}$ can be identified as arising from the excitation $t_{2g}^2 e_g^1 \leftarrow t_{2g}^3$ because the corresponding energy (close to 3 eV) is typical of ligand-field splittings in complexes.

Before we embark on a Racah-like analysis of the transition, it will be helpful to see qualitatively from the viewpoint of molecular orbital theory why the transition gives rise to two bands. First, note that a $d_z^2 \leftarrow d_{xy}$ transition, which is one way of achieving $e_g \leftarrow t_{2g}$, promotes an electron from the $xy$-plane into the already electron-rich $z$-direction: that axis is electron-rich because both $d_{yz}$ and $d_{zx}$ are occupied (Fig. 20.24). However, a $d_z^2 \leftarrow d_{z^2}$ transition, which is another way of achieving $e_g \leftarrow t_{2g}$, merely relocates an electron that is already largely concentrated along the $z$-axis. In the former case, but not in the latter, there is a distinct increase in electron repulsion and, as a result, the two $e_g \leftarrow t_{2g}$ transitions lie at different energies. There are six possible $t_{2g}^2 e_g^1 \leftarrow t_{2g}^3$ transitions, and all resemble one or other of these two cases: three of them fall into one group and the other three fall into the second group.

(b) The spectroscopic terms

**Key points:** The terms of an octahedral complex are labelled by the symmetry species of the overall orbital state; a superscript prefix shows the multiplicity of the term.

The two bands we are discussing in Fig. 20.22 are labelled $^4T_{2g} \leftarrow ^4A_{2g}$ (at 21 550 cm$^{-1}$) and $^4T_{1g} \leftarrow ^4A_{2g}$ (at 28 500 cm$^{-1}$). The labels are molecular term symbols and serve a

<table>
<thead>
<tr>
<th></th>
<th>1+</th>
<th>2+</th>
<th>3+</th>
<th>4+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>720 (3.7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>765 (3.9)</td>
<td>860 (4.8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>830 (4.1)</td>
<td>1030 (3.7)</td>
<td>1040 (4.1)</td>
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<tr>
<td>Mn</td>
<td>960 (3.5)</td>
<td>1130 (3.2)</td>
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<tr>
<td>Fe</td>
<td>1060 (4.1)</td>
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<tr>
<td>Co</td>
<td>1120 (3.9)</td>
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<tr>
<td>Ni</td>
<td>1080 (4.5)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Cu</td>
<td>1220 (4.0)</td>
<td>1240 (3.8)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The table gives the $B$ parameter in cm$^{-1}$ with the value of $C/B$ in parentheses.

$B$ and $C$. The values in parentheses indicate that $C = 4B$ so the ions listed there are in the region where Hund’s rules are not reliable for predicting anything more than the ground term of a configuration.

The parameter $C$ appears only in the expressions for the energies of states that differ in multiplicity from the ground state. Hence if, as is usual, we are interested only in the relative energies of terms of the same multiplicity as the ground state (that is excitation without a change in spin state), we do not need to know the value of $C$. The parameter $B$ is of the most interest, and we return to factors that affect its value in Section 20.4f.

20.4 Electronic spectra of complexes

The preceding discussion related only to free atoms, and we will now expand our discussion to encompass complex ions. The spectrum of $[\text{Cr(NH}_3)_6]^3-$ in Fig. 20.22 has two central bands with intermediate intensities and with energies that differ on account of the electron–electron repulsions (as we explain soon). Because both the transitions are between orbitals that are predominantly metal d orbital in character, with a separation characterized by the strength of the ligand-field splitting parameter $\Delta_{\text{t}_{2g}}$, these two transitions are called $d \leftarrow d$ transitions or ligand-field transitions.

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**Key point:** Electron–electron repulsion splits ligand-field transitions into components with different energies.

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Before we embark on a Racah-like analysis of the transition, it will be helpful to see qualitatively from the viewpoint of molecular orbital theory why the transition gives rise to two bands. First, note that a $d_z^2 \leftarrow d_{xy}$ transition, which is one way of achieving $e_g \leftarrow t_{2g}$, promotes an electron from the $xy$-plane into the already electron-rich $z$-direction: that axis is electron-rich because both $d_{yz}$ and $d_{zx}$ are occupied (Fig. 20.24). However, a $d_z^2 \leftarrow d_{z^2}$ transition, which is another way of achieving $e_g \leftarrow t_{2g}$, merely relocates an electron that is already largely concentrated along the $z$-axis. In the former case, but not in the latter, there is a distinct increase in electron repulsion and, as a result, the two $e_g \leftarrow t_{2g}$ transitions lie at different energies. There are six possible $t_{2g}^2 e_g^1 \leftarrow t_{2g}^3$ transitions, and all resemble one or other of these two cases: three of them fall into one group and the other three fall into the second group.

(b) The spectroscopic terms

**Key points:** The terms of an octahedral complex are labelled by the symmetry species of the overall orbital state; a superscript prefix shows the multiplicity of the term.

The two bands we are discussing in Fig. 20.22 are labelled $^4T_{2g} \leftarrow ^4A_{2g}$ (at 21 550 cm$^{-1}$) and $^4T_{1g} \leftarrow ^4A_{2g}$ (at 28 500 cm$^{-1}$). The labels are molecular term symbols and serve a

![Figure 20.24](image) The shifts in electron density that accompany the two transitions discussed in the text. There is a considerable relocation of electron density towards the ligands on the $z$-axis in (a), but a much less substantial relocation in (b).
The correlation of spectroscopic terms for d electrons in a d^1 complex with an electron in each of the three t_{2g} orbitals is denoted A_{1g}. We say nearly totally symmetrical because close inspection of the behaviour of the three occupied t_{2g} orbitals shows that the C_3 rotation of the O_h point group transforms the product t_{2g} × t_{2g} × t_{2g} into itself, which identifies the complex as an A_{1g} symmetry species (see the character table in Resource section 4). Moreover, because each orbital has even parity (g), the overall parity is also g. However, each C_4 rotation transforms one t_{2g} orbital into the negative of itself and the other two t_{2g} orbitals into each other (Fig. 20.25), so overall there is a change of sign under this operation and its character is −1. The term is therefore A_{2g}, rather than the totally symmetrical A_{1g} of a closed shell.

It is more difficult to establish that the term symbols that can arise from the quartet t_{2g}^2e_{1g} excited configuration are ^3T_{2g} and ^3T_{1g}, and we shall not consider this aspect here. The superscript 4 implies that the upper configuration continues to have the same number of unpaired spins as in the ground state, and the subscript g stems from the even parity of all the contributing orbitals.

(c) Correlating the terms

Key point: In the ligand field of an octahedral complex the free atom terms split and are then labelled by their symmetry species as enumerated in Table 20.8.

In a free atom, where all five d orbitals in a shell are degenerate, we needed to consider only the electron-electron repulsions to arrive at the relative ordering of the terms of a given d^1 configuration. In a complex, the d orbitals are not all degenerate and it is necessary to take into account the difference in energy between the t_{2g} and e_{1g} orbitals as well as the electron-electron repulsions.

Consider the simplest case of an atom or ion with a single valence electron. Because a totally symmetrical orbital in one environment becomes a totally symmetrical orbital in another environment, an s orbital in a free atom becomes an a_{1g} orbital in an octahedral field. We express the change by saying that the s orbital of the atom ‘correlates’ with the a_{1g} orbital of the complex. Similarly, the five d orbitals of a free atom correlate with the triply degenerate t_{2g} and doubly degenerate e_{1g} sets in an octahedral complex.

Now consider a many-electron atom. In exactly the same way as for a single electron, the totally symmetrical overall S term of a many-electron atom correlates with the totally symmetrical A_{1g} term of an octahedral complex. Likewise, an atomic D term splits into a T_{2g} term and an E term in O_h symmetry. The same kind of analysis can be applied to other states, and Table 20.8 summarizes the correlations between free atom terms and terms in an octahedral complex.

**EXAMPLE 20.7 Identifying correlations between terms**

What terms in a complex with O_h symmetry correlate with the ^4P term of a free atom with a d^1 configuration?

Answer We argue by analogy: if we know p orbitals correlate with orbitals in a complex, then we can use that information to express how the overall states correlate, simply by changing to uppercase letters. The three p orbitals of a free atom become the triply degenerate t_{2g} orbitals of an octahedral complex. Therefore, if we disregard parity for the moment, a P term of a many-electron atom becomes a T_{2g} term in the point group O_h. Because d orbitals have even parity, the term overall must be g, and specifically T_{1g}. The multiplicity is unchanged in the correlation, so the ^4P term becomes a ^3T_{1g} term.

Self-test 20.7 What terms in a d^1 complex of O_h symmetry correlate with the ^2F and ^2D terms of a free atom?

(d) The energies of the terms: weak- and strong-field limits

Key points: For a given metal ion, the energies of the individual terms respond differently to ligands of increasing field strength, and the correlation between free atom terms and terms of a complex can be displayed on an Orgel diagram.

Electron-electron repulsions are difficult to take into account, but the discussion is simplified by considering two extreme cases. In the weak-field limit the ligand field, as
measured by $\Delta_{O}$, is so weak that only electron–electron repulsions are important. As the Racah parameters $B$ and $C$ fully describe the interelectron repulsions, these are the only parameters we need at this limit. In the strong-field limit the ligand field is so strong that electron–electron repulsions can be ignored and the energies of the terms can be expressed solely in terms of $\Delta_{O}$. Then, with the two extremes established, we can consider intermediate cases by drawing a correlation diagram between the two. We shall illustrate what is involved by considering two simple cases, namely, $d^{1}$ and $d^{2}$. Then we show how the same ideas are used to treat more complicated cases.

The only term arising from the $d^{1}$ configuration of a free atom is $^{3}D$. In an octahedral complex the configuration is either $t_{2g}^{1}$, which gives rise to a $^{2}T_{2g}$ term, or $e_{g}^{1}$, which gives rise to a $^{2}E_{g}$ term. Because there is only one electron, there are no electron–electron repulsions to worry about, and the separation of the $^{2}T_{2g}$ and $^{2}E_{g}$ terms is the same as the separation of the $t_{2g}$ and $e_{g}$ orbitals, which is $\Delta_{O}$. The correlation diagram for the $d^{1}$ configuration will therefore resemble that shown in Fig. 20.26.

We saw earlier that for a $d^{2}$ configuration the lowest energy term in the free atom is the triplet $^{3}F$. We need consider only electronic transitions that start from the ground state, and, in this section, will discuss only those in which there is no change in spin. There is an additional triplet term ($^{3}P$); relative to the lower term ($^{1}F$), the energies of the terms are $E(^{3}F) = 0$ and $E(^{3}P) = 15B$. These two energies are marked on the left of Fig. 20.27. Now consider the very strong-field limit. A $d^{2}$ atom has the configurations

$$t_{2g}^{3} < t_{2g}^{1}e_{g} < e_{g}^{2}$$

In an octahedral field, these configurations have different energies; that is, as we noted earlier, the $^{3}F$ term splits into three terms. From the information in Fig. 20.2, we can write their energies as

$$E(t_{2g}^{3}) = 2(-\frac{2}{3}\Delta_{O}) = -0.8\Delta_{O}$$

$$E(t_{2g}^{1}e_{g}) = (-\frac{2}{3} + \frac{2}{3})\Delta_{O} = +0.2\Delta_{O}$$

$$E(e_{g}^{2}) = 2(\frac{2}{3})\Delta_{O} = +1.2\Delta_{O}$$

Therefore, relative to the energy of the lowest term, their energies are

$$E(t_{2g}^{3}, T_{1g}) = 0 \quad E(t_{2g}^{1}e_{g}, T_{2g}) = \Delta_{O} \quad E(e_{g}^{2}, A_{2g}) = 2\Delta_{O}$$

These energies are marked on the right in Fig. 20.27.

Our problem now is to account for the energies when neither the ligand-field nor the electron repulsion terms is dominant. To do so, we correlate the terms in the two extreme cases. The triplet $t_{2g}^{3}$ configuration gives rise to a $^{3}T_{1g}$ term, and this correlates with the $^{3}F$ term of the free atom. The remaining correlations can be established similarly, and we see that the $t_{2g}^{1}e_{g}$ configuration gives rise to a $^{3}T_{2g}$ term and that the $e_{g}^{2}$ configuration gives rise to a $A_{2g}$ term; both terms correlate with the $^{3}F$ term of the free atom. Note that some terms, such as the $^{3}T_{1g}$ term that correlates with $^{3}P$, are independent of the ligand-field strength. All the correlations are shown in Fig. 20.27, which is a simplified version of an Orgel diagram. An Orgel diagram can be constructed for any $d$-electron configuration, and several electronic configurations can be combined on the same diagram. Orgel diagrams are of considerable value for simple discussions of the electronic spectra of complexes; however, they consider only some of the possible transitions (the spin-allowed transitions, which is why we considered only the triplet terms) and cannot be used to extract a value for the ligand-field splitting parameter, $\Delta_{O}$.

(e) Tanabe–Sugano diagrams

**Key point:** Tanabe–Sugano diagrams are correlation diagrams that depict the energies of electronic states of complexes as a function of the strength of the ligand field.

Diagrams showing the correlation of all terms can be constructed for any electron configuration and strength of ligand field. The most widely used versions are called Tanabe–Sugano diagrams, after the scientists who devised them. Figure 20.28 shows the diagram for $d^{2}$ and we can see splittings for all the atomic terms that split; thus the $^{3}F$ splits into three, the $^{3}D$ into two, and the $^{3}G$ into four. In these diagrams the term energies, $E$, are expressed as $E/B$ and plotted against $\Delta_{O}/B$, where $B$ is the Racah parameter. The relative energies of the
terms arising from a given configuration are independent of \(A\), and by choosing a value of \(C\) (typically setting \(C = 4B\)), terms of all energies can be plotted on the same diagrams. Some lines in Tanabe–Sugano diagrams are curved because of the mixing of terms of the same symmetry type. Terms of the same symmetry obey the **noncrossing rule**, which states that, if the increasing ligand field causes two weak-field terms of the same symmetry to approach, then they do not cross but bend apart from each other (Fig. 20.29). The effect of the noncrossing rule can be seen for the two \(^1E\) terms, the two \(^1T_2\) terms, and the two \(^1A_1\) terms in Fig. 20.28.

Tanabe–Sugano diagrams for \(O_\text{a}\) complexes with configurations \(d^2\) to \(d^9\) are given in Resource section 6. The zero of energy in a Tanabe–Sugano diagram is always taken as that of the lowest term. Hence the lines in the diagrams have abrupt changes of slope when there is a change in the identity of the ground term brought about by the change from high-spin to low-spin with increasing field strength (see the diagram for \(d^4\), for instance).

The purpose of the preceding discussion has been to find a way to extract the value of the ligand-field splitting parameter from the electronic absorption spectrum of a complex with more than one d electron, when electron–electron repulsions are important, such as that in Fig. 20.22. The strategy involves fitting the observed transitions to the correlation lines in a Tanabe–Sugano diagram and identifying the values of \(\Delta_0\) and \(B\) where the observed transition energies match the pattern. This procedure is illustrated in Example 20.8.

As we shall see in Section 20.6, certain transitions are allowed and certain transitions are forbidden. In particular, those that correspond to a change of spin state are forbidden, whereas those that do not are allowed. In general, spin-allowed transitions will dominate the UV/visible absorption spectrum, thus we might only expect to see three transitions for a \(d^3\) ion, specifically \(^4T_{2g} ← ^4A_{2g}\), \(^4T_{1g} ← ^4T_{1g}\), and \(^4A_{2g} ← ^4T_{1g}\). However, some complexes (for instance high-spin \(d^3\) ions such as Mn(II)) do not have any spin-allowed transitions and none of the 11 possible transitions dominates.

### Example 20.8 Calculating \(\Delta_0\) and \(B\) using a Tanabe–Sugano diagram

Deduce the values of \(\Delta_0\) and \(B\) for \([\text{Cr}(\text{NH}_3)_6]^{3+}\) from the spectrum in Fig. 20.22 and a Tanabe–Sugano diagram.

**Answer** We need to identify the relevant Tanabe–Sugano diagram and then locate the position on the diagram where the observed ratio of transition energies (as wavenumbers) matches the theoretical ratio. The relevant diagram (for \(d^3\)) is shown in Fig. 20.30. We need concern ourselves only with the spin-allowed transitions, of which there are three for a \(d^3\) ion (a \(^4T_{2g} ← ^4A_{2g}\) and two \(^4T_{1g} ← ^4A_{2g}\) transitions). We have seen that the spectrum in Fig. 20.22 exhibits two low-energy ligand-field transitions at 21 550 and 28 500 cm\(^{-1}\), which correspond to the two lowest energy transitions (\(^4T_{2g} ← ^4A_{2g}\) and \(^4T_{1g} ← ^4A_{2g}\)). The ratio of the energies of the transitions is 1.32, and the only point in Fig. 20.30 where this energy ratio is satisfied is on the far right. Hence, we can read off the value of \(\Delta_0/B = 33.0\) from the location of this point. The tip of the arrow representing the lower energy transition lies at 32.88 vertically, so equating 32.88 and 21 550 cm\(^{-1}\) gives \(B = 657\) cm\(^{-1}\) and therefore \(\Delta_0 = 21 700\) cm\(^{-1}\).

**Selftest 20.8** Use the same Tanabe–Sugano diagram to predict the energy of the first spin-allowed quartet bands in the spectrum of \([\text{Cr}(\text{OH}_3)_6]^{3+}\) for which \(\Delta_0 = 17 600\) cm\(^{-1}\) and \(B = 700\) cm\(^{-1}\).

A Tanabe–Sugano diagram also provides some information about the widths of some absorption lines. Consider Fig. 20.28 and the \(^4T_{2g} ← ^4T_{1g}\) and \(^4A_{2g} ← ^4T_{1g}\) transitions. The line representing \(^4T_{2g}\) is not parallel to that representing the ground state \(^4T_{1g}\), and so any variation in the value of \(\Delta_0\) (such as those caused by molecular vibration) results in a change in the energy of the transition and thus a broadening of the absorption band. The line representing \(^4A_{2g}\) is even less parallel to the line representing \(^4T_{1g}\); the energy of this transition will be affected even more by variations in \(\Delta_0\) and will thus be even broader. By contrast, the line representing the lower \(^4T_{2g}\) term is almost parallel to that representing \(^4T_{1g}\), and thus the energy of this transition is largely unaffected by variations in \(\Delta_0\), and the absorption is consequently very sharp (albeit weak, because it is forbidden).

(f) The nephelauxetic series

**Key points:** Electron–electron repulsions are lower in complexes than in free ions because of electron delocalization; the nephelauxetic parameter is a measure of the extent of d-electron delocalization on to the ligands of a complex; the softer the ligand, the smaller the nephelauxetic parameter.
In Example 20.8 we found that \( B = 657 \text{ cm}^{-1} \) for \([\text{Cr(NH}_3\text{)}_6]^{3+}\), which is only 64 per cent of the value for a Cr\(^{3+}\) ion in the gas phase. This reduction is a general observation and indicates that electron repulsions are weaker in complexes than in the free atoms and ions. The weakening occurs because the occupied molecular orbitals are delocalized over the ligands and away from the metal. The delocalization increases the average separation of the electrons and hence reduces their mutual repulsion.

The reduction of \( B \) from its free ion value is normally reported in terms of the **nephelauxetic parameter**, \( \beta \):\(^4\)

\[
\beta = \frac{B(\text{complex})}{B(\text{free ion})}
\]

(20.4)

The values of \( \beta \) depend on the identity of the metal ion and the ligand, and a list of ligands ordered by the value of \( \beta \) gives the **nephelauxetic series**: \[
\text{Br}^- < \text{CN}^- < \text{Cl}^- < \text{NH}_3 < \text{H}_2\text{O} < \text{F}^-\]

A small value of \( \beta \) indicates a large measure of d-electron delocalization on to the ligands and hence a significant covalent character in the complex. Thus the series shows that a Br\(^-\) ligand results in a greater reduction in electron repulsions in the ion than an F\(^-\) ion, which is consistent with a greater covalent character in bromido complexes than in analogous fluorido complexes. An example, compare \([\text{NiF}_3]^{3+}\), for which \( B = 843 \text{ cm}^{-1} \), with \([\text{NiBr}_3]^{3+}\), for which \( B = 600 \text{ cm}^{-1} \). Another way of expressing the trend represented by the nephelauxetic series is: **the softer the ligand, the smaller the nephelauxetic parameter.**

### 20.5 Charge-transfer bands

**Key points:** Charge-transfer bands arise from the movement of electrons between orbitals that are predominantly ligand in character and orbitals that are predominantly metal in character; such transitions are identified by their high intensity and the sensitivity of their energies to solvent polarity.

Another feature in the spectrum of \([\text{Cr(NH}_3\text{)}_6]^{3+}\) in Fig. 20.22 that remains to be explained is the very intense shoulder of an absorption that appears to have a maximum at well above 50 000 cm\(^{-1}\). The high intensity suggests that this transition is not a simple ligand-field transition, but is consistent with a **charge-transfer transition** (CT transition). In a CT transition, an electron migrates between orbitals that are predominantly ligand in character and orbitals that are predominantly metal in character. The transition is classified as a **ligand-to-metal charge-transfer transition** (LMCT transition) if the migration of the electron is from the ligand to the metal, and as a **metal-to-ligand charge-transfer transition** (MLCT transition) if the charge migration occurs in the opposite direction. An example of an MLCT transition is the one responsible for the red colour of tris(bipyridyl)iron(II), the complex used for the colorimetric analysis of Fe(II). In this case, an electron makes a transition from a d orbital of the central metal into a \( \pi^* \) orbital of the ligand. Figure 20.31 summarizes the transitions we classify as charge transfer.

Several lines of evidence are used to identify a band as due to a CT transition. The high intensity of the band, which is evident in Fig. 20.22, is one strong indication. Another indication is if such a band appears following the replacement of one ligand with another, as this implies that the band is strongly dependent on the ligand. The CT character is most often identified (and distinguished from \( \pi^* \leftarrow \pi \) transitions on ligands) by demonstrating **solvatochromism**, the variation of the transition frequency with changes in solvent permittivity. Solvatochromism indicates that there is a large shift in electron density as a result of the transition, which is more consistent with a metal–ligand transition than a ligand–ligand or metal–metal transition.

Figure 20.32 shows another example of a CT transition in the visible and UV spectrum of \([\text{CrCl(NH}_3\text{)}_6]^{3+}\) (5). If we compare this spectrum with that of \([\text{Cr(NH}_3\text{)}_6]^{3+}\) in Fig. 20.22, then we can recognize the two ligand-field bands in the visible region. The replacement of one NH\(_3\) ligand by a weaker field Cl\(^-\) ligand moves the lowest energy ligand-field bands to lower energy than those of \([\text{Cr(NH}_3\text{)}_6]^{3+}\). Also, a shoulder appears on the high-energy side of one of the ligand-field bands, indicating an additional transition that is the result of the reduction in symmetry from \( O_h \) to \( C_{3v} \). The major new feature in the spectrum is the strong absorption maximum in the ultraviolet, near 42 000 cm\(^{-1}\). This band is at lower energy than the corresponding band in the spectrum of \([\text{Cr(NH}_3\text{)}_6]^{3+}\) and is due to an

\(^4\)The name is from the Greek words for ‘cloud expanding’.
A LMCT transition from the Cl\(^{-}\) ligand to the metal. The LMCT character of similar bands in [CoX(NH\(_3\)]\(^{2+}\) is confirmed by the decrease in energy in steps of about 8000 cm\(^{-1}\) as X is varied from Cl to Br to I. In this LMCT transition, a lone-pair electron of the halide ligand is promoted into a predominantly metal orbital.

(a) LMCT transitions

**Key points:** Ligand-to-metal charge-transfer transitions are observed in the visible region of the spectrum when the metal is in a high oxidation state and ligands contain nonbonding electrons; the variation in the position of LMCT bands can be parameterized in terms of optical electronegativities.

Charge-transfer bands in the visible region of the spectrum (and hence contributing to the intense colours of many complexes) may occur if the ligands have lone pairs of relatively high energy (as in sulfur and selenium) or if the metal atom has low-lying empty orbitals.

The tetraoxidoanions of metals with high oxidation numbers (such as MnO\(_4\)) provide what are probably the most familiar examples of LMCT bands. In these, an O lone-pair electron is promoted into a low-lying empty metal e orbital. High metal oxidation numbers correspond to a low d-orbital population (many are formally d\(^0\)), so the acceptor level is available and low in energy. The trend in LMCT energies is:

\[
\begin{align*}
\text{Oxidation number} & \\
+7 & \text{MnO}_4^- < \text{TcO}_4^- < \text{ReO}_4^- \\
+6 & \text{CrO}_4^{2-} < \text{MoO}_4^{2-} < \text{WO}_4^{2-} \\
+5 & \text{V}_2\text{O}_7^{2-} < \text{Nb}_2\text{O}_7^{2-} < \text{Ta}_2\text{O}_7^{2-}
\end{align*}
\]

The UV/visible spectra of the tetraoxido anions of the Group 6 metals, CrO\(_4^{2-}\), MoO\(_4^{2-}\), and WO\(_4^{2-}\) are shown in Fig. 20.33. The energies of the transitions correlate with the order of the electrochemical series, with the lowest energy transitions taking place to the most easily reduced metal ions. This correlation is consistent with the transition being the transfer of an electron from the ligands to the metal ion, corresponding, in effect, to the reduction of the metal ion by the ligands. Polymeric and monomeric oxidoanions follow the same trends, with the oxidation state of the metal the determining factor. The similarity suggests that these LMCT transitions are localized processes that take place on discrete molecular fragments.

The variation in the position of LMCT bands can be expressed in terms of the optical electronegativities of the metal, \(\chi_{\text{metal}}\), and the ligands, \(\chi_{\text{ligand}}\). The wavenumber of the transition is then written as the difference between the two electronegativities:

\[
\tilde{\nu} = |\chi_{\text{ligand}} - \chi_{\text{metal}}| \tilde{\nu}_o
\]

Optical electronegativities have values comparable to Pauling electronegativities (Table 1.7) if we set \(\tilde{\nu}_o = 3.0 \times 10^4 \text{ cm}^{-1}\) (Table 20.9), and can be used in a similar fashion. If the LMCT transition terminates in an \(e_g\) orbital, \(\Delta_0\) must be added to the energy predicted by this equation. Electron pairing energies must also be taken into account if the transition results in the population of an orbital that already contains an electron. The values for metals are different in complexes of different symmetry, and the ligand values are different if the transition originates from a \(\pi\) orbital rather than a \(\sigma\) orbital.

**Table 20.9 Optical electronegativities**

<table>
<thead>
<tr>
<th>Metal</th>
<th>(Q_o)</th>
<th>(T_g)</th>
<th>Ligand</th>
<th>(\pi)</th>
<th>(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(III)</td>
<td>1.8–1.9</td>
<td>F(^{-})</td>
<td>3.9</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>Co(III)*</td>
<td>2.3</td>
<td>Cl(^{-})</td>
<td>3.0</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Ni(II)*</td>
<td>2.0–2.1</td>
<td>Br(^{-})</td>
<td>2.8</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>Co(II)</td>
<td>1.8–1.9</td>
<td>I(^{-})</td>
<td>2.5</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Rh(III)*</td>
<td>2.3</td>
<td>H(_2)O</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(VI)</td>
<td>2.1</td>
<td>NH(_3)</td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Low-spin complexes.
(b) MLCT transitions

**Key point:** Charge-transfer transitions from metal to ligand are observed when the metal is in a low oxidation state and the ligands have low-lying acceptor orbitals.

Charge-transfer transitions from metal to ligand are most commonly observed in complexes with ligands that have low-lying π* orbitals, especially aromatic ligands. The transition occurs at low energy and appears in the visible spectrum if the metal ion is in a low oxidation state, as its d orbitals are then relatively close in energy to the empty ligand orbitals.

The family of ligands most commonly involved in MLCT transitions are the diimines, which have two N donor atoms: two important examples are 2,2′-bipyridine (bpy, 6) and 1,10-phenanthroline (phen, 7). Complexes of diimines with strong MLCT bands include tris(diimine) species such as tris(2,2′-bipyridyl)ruthenium(II) (8), which is orange. A diimine ligand may also be easily substituted into a complex with other ligands that favour a low oxidation state. Two examples are [W(CO)₅(phen)] and [Fe(CO)₅(bpy)]. However, the occurrence of MLCT transitions is by no means limited to diimine ligands. Another important ligand type that shows typical MLCT transitions is dithiolene, S₂C₆R₂⁺ (9). Resonance Raman spectroscopy (Section 8.4) is a powerful technique for the study of MLCT transitions.

The MLCT excitation of tris(2,2′-bipyridyl)ruthenium(II) has been the subject of intense research efforts because the excited state that results from the charge transfer has a lifetime of microseconds, and the complex is a versatile photochemical redox reagent. The photochemical behaviour of a number of related complexes has also been studied on account of their relatively long excited-state lifetimes.

### 20.6 Selection rules and intensities

**Key point:** The strength of an electronic transition is determined by the transition dipole moment.

The contrast in intensity between typical charge-transfer bands and typical ligand-field bands raises the question of the factors that control the intensities of absorption bands. In an octahedral, nearly octahedral, or square-planar complex, the maximum molar absorption coefficient εₘₐₓ (which measures the strength of the absorption) is typically less than or close to 100 dm⁻¹ mol⁻¹ cm⁻¹ for ligand-field transitions. In tetrahedral complexes, which have no centre of symmetry, εₘₐₓ for ligand-field transitions might exceed 250 dm⁻¹ mol⁻¹ cm⁻¹. By contrast, charge-transfer bands usually have an εₘₐₓ in the range 1000–50 000 dm⁻¹ mol⁻¹ cm⁻¹.

To understand the intensities of transitions in complexes we have to explore the strength with which the complex couples with the electromagnetic field. Intense transitions indicate strong coupling; weak transitions indicate feeble coupling. The strength of coupling when an electron makes a transition from a state with wavefunction ψᵣ to one with wavefunction ψᵢ is measured by the transition dipole moment, which is defined as the integral

\[ \mu_n = \int \psi_i^* \mu \psi_r \, d\tau \]  

(20.5)

where \( \mu \) is the electric dipole moment operator, \( -er \). The transition dipole moment can be regarded as a measure of the impulse that a transition imparts to the electromagnetic field: a large impulse corresponds to an intense transition; zero impulse corresponds to a forbidden transition. The intensity of a transition is proportional to the square of its transition dipole moment.

A spectroscopic selection rule is a statement about which transitions are allowed and which are forbidden. An allowed transition is a transition with a nonzero transition dipole moment, and hence nonzero intensity. A forbidden transition is a transition for which the transition dipole moment is calculated as zero. Formally forbidden transitions may occur in a spectrum if the assumptions on which the transition dipole moment were calculated are invalid, such as the complex having a lower symmetry than assumed.

The molar absorption coefficient is the constant in the Beer–Lambert law for the transmittance \( T = I/I_0 \), when light passes through a length \( L \) of solution of molar concentration \( [X] \) and is attenuated from an intensity \( I_0 \) to an intensity \( I \): log \( T = -\varepsilon[X]L \) (the logarithm is a common logarithm, to the base 10). Its older but still widely used name is the ‘extinction coefficient’.
(a) Spin selection rules

**Key points:** Electronic transitions with a change of multiplicity are forbidden; intensities of spin-forbidden transitions are greater for 4d- or 5d-series metal complexes than for comparable 3d-series complexes.

The electromagnetic field of the incident radiation cannot change the relative orientations of the spins of the electrons in a complex. For example, an initially antiparallel pair of electrons cannot be converted to a parallel pair, so a singlet \( S = 0 \) cannot undergo a transition to a triplet \( S = 1 \). This restriction is summarized by the rule \( \Delta S = 0 \) for spin-allowed transitions, Fig. 20.34.

The coupling of spin and orbital angular momenta can relax the spin selection rule, but such spin-forbidden, \( \Delta S \neq 0 \), transitions are generally much weaker than spin-allowed transitions. The intensity of spin-forbidden bands increases as the atomic number increases because the strength of the spin-orbit coupling is greater for heavy atoms than for light atoms. The breakdown of the spin selection rule by spin-orbit coupling is often called the heavy-atom effect. In the 3d series, in which spin-orbit coupling is weak, spin-forbidden bands have \( \varepsilon_{\text{max}} \) less than about 1 \( \text{dm}^3\text{mol}^{-1}\text{cm}^{-1} \); however, spin-forbidden bands are a significant feature in the spectra of heavy d-metal complexes.

The very weak transition labelled \( ^2\text{E} \leftarrow ^4\text{A}_g \) in Fig. 20.22 is an example of a spin-forbidden transition. Some metal ions, such as the \(^{3}\text{Mn}^{2+} \) ion, have no spin-allowed transitions, and hence are only weakly coloured.

(b) The Laporte selection rule

**Key points:** Transitions between d orbitals are forbidden in octahedral complexes; asymmetric vibrations relax this restriction.

The Laporte selection rule states that in a centrosymmetric molecule or ion, the only allowed transitions are those accompanied by a change in parity. That is, transitions between g and u terms are permitted, but a g term cannot undergo a transition to another g term and a u term cannot undergo a transition to another u term:

\[
g \leftrightarrow u \quad g \not\leftrightarrow g \quad u \not\leftrightarrow u
\]

In many cases it is enough to note that in a centrosymmetric complex, if there is no change in quantum number \( l \), then there can be no change in parity. Thus, \( s \leftrightarrow s \), \( p \leftrightarrow p \), \( d \leftrightarrow d \), and \( f \leftrightarrow f \) transitions are forbidden. Since \( s \) and \( d \) orbitals are g, whereas \( p \) and \( f \) orbitals are u it follows that \( s \leftrightarrow p \), \( p \leftrightarrow d \), and \( d \leftrightarrow f \) transitions are allowed whereas \( s \leftrightarrow d \) and \( p \leftrightarrow f \) transitions are forbidden.

A more formal treatment of the Laporte selection rule is based on the properties of the transition dipole moment, which is proportional to \( r \). Because \( r \) changes sign under inversion (and is therefore u), the entire integral in eqn 20.5 also changes sign under inversion if \( \phi_i \) and \( \phi_j \) have the same parity because \( g \times u \times g = u \) and \( u \times u \times u = u \). Therefore, because the value of an integral cannot depend on the choice of coordinates used to evaluate it,\(^6\) it vanishes if \( \phi_i \) and \( \phi_j \) have the same parity. However, if they have opposite parity, the integral does not change sign under inversion of the coordinates because \( g \times u \times u = g \) and therefore need not vanish.

In a centrosymmetric complex, \( d \leftrightarrow d \) ligand-field transitions are g \( \leftrightarrow \) g and are therefore forbidden. Their forbidden character accounts for the relative weakness of these transitions in octahedral complexes (which are centrosymmetric) compared with those in tetrahedral complexes, on which the Laporte rule is silent (they are noncentrosymmetric, and have no g or u as a subscript).

The question remains why \( d \leftrightarrow d \) ligand-field transitions in octahedral complexes occur at all, even weakly. The Laporte selection rule may be relaxed in two ways. First, a complex may depart slightly from perfect centrosymmetry in its ground state, perhaps on account of the intrinsic asymmetry in the structure of polyatomic ligands or a distortion imposed by the environment of a complex packed into a crystal. Alternatively, the complex might undergo an asymmetrical vibration, which also destroys its centre of inversion. In either case, a Laporte-forbidden \( d \leftrightarrow d \) ligand-field band tends to be much more intense than a spin-forbidden transition.

\(^6\)An integral is an area, and areas are independent of the coordinates used for their evaluation.
Table 20.10 summarizes typical intensities of electronic transitions of complexes of the 3d-series elements. The width of spectroscopic absorption bands is due principally to the simultaneous excitation of vibration when the electron is promoted from one distribution to another. According to the Franck–Condon principle, the electronic transition takes place within a stationary nuclear framework. As a result, after the transition has occurred, the nuclei experience a new force field and the molecule begins to vibrate anew.

**EXAMPLE 20.9 Assigning a spectrum using selection rules**

Assign the bands in the spectrum in Fig. 20.32 by considering their intensities.

**Answer** If we assume that the complex is approximately octahedral, examination of the Tanabe–Sugano diagram for a $d^1$ ion reveals that the ground term is $^{4}A_{2g}$. Transitions to the higher terms $^{2}E_g$, $^{2}T_{1g}$, and $^{2}T_{2g}$ are spin-forbidden and will have $\varepsilon_{\text{max}} < 1 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Thus, very weak bands for these transitions are predicted, and will be difficult to distinguish. The next two higher terms of the same multiplicity are $^{4}T_{2g}$ and $^{4}T_{1g}$. These terms are reached by spin-allowed but Laporte-forbidden ligand-field transitions, and have $\varepsilon_{\text{max}} \approx 100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$: these are the two bands at 360 and 510 nm. In the near UV, the band with $\varepsilon_{\text{max}} = 10 000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ corresponds to the LMCT transitions in which an electron from a chlorine $\pi$ lone pair is promoted into a molecular orbital that is principally metal $d$ orbital in character.

**Self-test 20.9** The spectrum of $\text{[Cr(NCS)}_3\text{]}^-$ has a very weak band near 16 000 cm$^{-1}$, a band at 17 700 cm$^{-1}$ with $\varepsilon_{\text{max}} = 160 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, a band at 23 800 cm$^{-1}$ with $\varepsilon_{\text{max}} = 130 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, and a very strong band at 32 400 cm$^{-1}$. Assign these transitions using the $d^1$ Tanabe–Sugano diagram and selection rule considerations. (Hint: NCS$^-$ has low-lying $\pi^*$ orbitals.)

### 20.7 Luminescence

**Key points:** A luminescent complex is one that re-emits radiation after it has been electronically excited. Fluorescence occurs when there is no change in multiplicity, whereas phosphorescence occurs when an excited state undergoes intersystem crossing to a state of different multiplicity and then undergoes radiative decay.

A complex is luminescent if it emits radiation after it has been electronically excited by the absorption of radiation. Luminescence competes with nonradiative decay by thermal degradation of energy to the surroundings. Relatively fast radiative decay is not especially common at room temperature for $d$-metal complexes, so strongly luminescent systems are comparatively rare. Nevertheless, they do occur, and we can distinguish two types of process. Traditionally, rapidly decaying luminescence was called ‘fluorescence’ and luminescence that persists after the exciting illumination is extinguished was called ‘phosphorescence’. However, because the lifetime criterion is not reliable, the modern definitions of the two kinds of luminescence are based on the distinctive mechanisms of the processes.

**Fluorescence** is radiative decay from an excited state of the same multiplicity as the ground state. The transition is spin-allowed and is fast; fluorescence half-lives are a matter of nanoseconds. **Phosphorescence** is radiative decay from a state of different multiplicity from the ground state. It is a spin-forbidden process, and hence is often slow.

The initial excitation of a phosphorescent complex usually populates a state by a spin-allowed transition, so the mechanism of phosphorescence involves intersystem crossing, the nonradiative conversion of the initial excited state into another excited state of different multiplicity. This second state acts as an energy reservoir because radiative decay to the ground state is spin-forbidden. However, just as spin–orbit coupling allows the intersystem crossing to occur, it also breaks down the spin selection rule, so the radiative decay can occur. Radiative decay back to the ground state is slow, so a phosphorescent state of a $d$-metal complex may survive for microseconds or even longer.

An important example of phosphorescence is provided by ruby, which consists of a low concentration of $\text{Cr}^{3+}$ ions in place of $\text{Al}^{3+}$ in alumina. Each $\text{Cr}^{3+}$ ion is surrounded octahedrally by six $\text{O}^{2-}$ ions and the initial excitations are the spin-allowed processes

$$t_{2g}^2e_{g}^1 \rightarrow t_{2g}^{1.5} \quad T_{2g} \leftarrow 4A_{2g} \quad \text{and} \quad T_{1g} \leftarrow 4A_{2g}$$

These absorptions occur in the green and violet regions of the spectrum and are responsible for the red colour of the gem (Fig. 20.35). Intersystem crossing to a $^4\text{E}$ term of the $t_{2g}^{1.5}$ configuration occurs in a few picoseconds or less, and red 627 nm phosphorescence occurs...
as this doublet decays back into the quartet ground state. This red emission adds to the red perceived by the subtraction of green and violet light from white light, and adds lustre to the gem’s appearance. This effect was utilised in the first laser to be constructed (in 1960).

A similar \( ^2E \rightarrow ^4A \) phosphorescence can be observed from a number of Cr(III) complexes in solution. The \( ^2E \) term arises from the \( t_{2g}^3 \) configuration, which is the same as the ground state, and thus the strength of the ligand field is not important. Hence the emission is always in the red (and close to the wavelength of ruby emission). If the ligands are rigid, as in \([\text{Cr(bpy)}_3]^3+\), the \(^2E\) term may live for several microseconds in solution.

Another interesting example of a phosphorescent state is found in \([\text{Ru(bpy)}_3]^2+\). The excited singlet term produced by a spin-allowed MLCT transition of this \(d^6\) complex undergoes intersystem crossing to the lower energy triplet term of the same configuration, \(t_{2g}^2\pi^1\). Bright orange emission then occurs with a lifetime of about 1 \(\mu\)s (Fig. 20.36). The effects of other molecules (quenchers) on the lifetime of the emission may be used to monitor the rate of electron transfer from the excited state.

### Magnetism

The diamagnetic and paramagnetic properties of complexes were introduced in Section 20.1c, but the discussion was restricted to magnetically dilute species, where the individual paramagnetic centres, the atoms with unpaired d-electrons, are separate from each other. We now consider two further aspects of magnetism, one where magnetic centres can interact with one another and one where the spin-state may change.

#### 20.8 Cooperative magnetism

**Key point:** In solids, the spins on neighbouring metal centres may interact to produce magnetic behaviour, such as ferromagnetism and antiferromagnetism, that are representative of the whole solid.

In the solid state the individual magnetic centres are often close together and separated by only a single atom, typically O. In such arrays cooperative properties can arise from interactions between electron spins on different atoms.

The magnetic susceptibility, \(\chi\), of a material is a measure of how easy it is to align electron spins with the applied magnetic field in the sense that the induced magnetic moment is proportional to the applied field, with \(\chi\) the constant of proportionality. A paramagnetic material has a positive susceptibility and a diamagnetic material has a negative susceptibility. Magnetic effects arising from cooperative phenomena can be very much larger than those arising from individual atoms and ions. The susceptibility and its variation with temperature are different for different types of magnetic materials and are summarized in Table 20.11 and Fig. 20.37.

The application of a magnetic field to a paramagnetic material results in the partial alignment of the spins parallel to the field. As a paramagnetic material is cooled, the disordered effect of thermal motion is reduced, more spins become aligned, and the magnetic susceptibility increases. In a **ferromagnetic substance**, which is one example of a cooperative magnetic property, the spins on different metal centres are coupled into a parallel alignment that is sustained over thousands of atoms to form a **magnetic domain** (Fig. 20.38). The net magnetic moment, and hence the magnetic susceptibility, may be

### Table 20.11 Magnetic behaviour of materials

<table>
<thead>
<tr>
<th>Magnetic behaviour</th>
<th>Typical value of (\chi)</th>
<th>Variation of (\chi) with temperature</th>
<th>Field dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetism (no unpaired spins)</td>
<td>(-8 \times 10^{-6}) for Cu</td>
<td>None</td>
<td>No</td>
</tr>
<tr>
<td>Paramagnetism</td>
<td>(4 \times 10^{-1}) for FeSO(_4)</td>
<td>Decreases</td>
<td>No</td>
</tr>
<tr>
<td>Ferromagnetism</td>
<td>(5 \times 10^{1}) for Fe</td>
<td>Decreases</td>
<td>Yes</td>
</tr>
<tr>
<td>Antiferromagnetism</td>
<td>(0 - 10^{-2})</td>
<td>Increases</td>
<td>(Yes)</td>
</tr>
</tbody>
</table>
very large because the magnetic moments of individual spins add to each other. Moreover, once established and with the temperature maintained below the Curie temperature ($T_c$), the magnetization persists after the applied field is removed because the spins are locked together. Ferromagnetism is exhibited by materials containing unpaired electrons in d or, more rarely, f orbitals that couple with unpaired electrons in similar orbitals on surrounding atoms. The key feature is that this interaction is strong enough to align spins but not so strong as to form covalent bonds, in which the electrons would be paired. At temperatures above $T_c$ the disordering effect of thermal motion overcomes the ordering effect of the interaction and the material becomes paramagnetic (Fig. 20.37).

The magnetization, $M$, of a ferromagnet, its bulk magnetic moment, is not proportional to the applied field strength $H$. Instead, a ‘hysteresis loop’ is observed like that shown in Fig. 20.39. For hard ferromagnets the loop is broad and $M$ remains large when the applied field has been reduced to zero. Hard ferromagnets are used for permanent magnets where the direction of the magnetization does not need to be reversed. A soft ferromagnet has a narrower hysteresis loop and is therefore much more responsive to the applied field. Soft ferromagnets are used in transformers, where they must respond to a rapidly oscillating field.

In an antiferromagnetic material, neighbouring spins are locked into an antiparallel alignment (Fig. 20.40). As a result, the collection of individual magnetic moments cancel and the sample has a low magnetic moment and magnetic susceptibility (tending, in fact, to zero). Antiferromagnetism is often observed when a paramagnetic material is cooled to a low temperature and is indicated by a sharp decrease in magnetic susceptibility at the Néel temperature, $T_N$ (Fig. 24.37). Above $T_N$ the magnetic susceptibility is that of a paramagnetic material, and decreases as the temperature is raised.

The spin coupling responsible for antiferromagnetism generally occurs through intervening ligands by a mechanism called superexchange. As indicated in Fig. 20.41, the spin on one metal atom induces a small spin polarization on an occupied orbital of a ligand, and this spin polarization results in an antiparallel alignment of the spin on the adjacent metal atom. This alternating $\uparrow \downarrow \uparrow \downarrow \ldots$ alignment of spins then propagates throughout the material. Many d-metal oxides exhibit antiferromagnetic behaviour that can be ascribed to a superexchange mechanism involving O atoms, for example MnO is antiferromagnetic below 122 K and Cr$_2$O$_3$ is antiferromagnetic below 310 K. Coupling of spins through intervening ligands is frequently observed in molecular complexes containing two ligand-bridged metal ions but it is weaker than with a simple O$^-$ link between metal sites and as a result the ordering temperatures are much lower, typically below 100 K.

In ferrimagnetism, a net magnetic ordering of ions with different individual magnetic moments is observed below the Curie temperature. These ions can order with opposed spins, as in antiferromagnetism, but because the individual spin moments are different, there is incomplete cancellation and the sample has a net overall moment. As with antiferro-magnetism, these interactions are generally transmitted through the ligands; an example is magnetite Fe$_3$O$_4$.

There are a large number of molecular systems where magnetic coupling is observed. Typical systems have two or more metal atoms bridged by ligands that mediate the coupling. Simple examples include copper acetate (10), which exists as a dimer with antiferromagnetic coupling between the two d$^9$ centres. Many metalloenzymes (Sections 27.9 to 27.14) have multiple metal centres that show magnetic coupling.
20 d-Metal complexes: electronic structure and properties

20.9 Spin crossover complexes

Key point: When the factors that determine the spin state of a d-metal centre are closely matched, complexes that change spin state in response to external stimuli are possible.

We have seen how a number of factors, such as oxidation state and ligand type, determine whether a complex is high- or low-spin. With some complexes, normally of the 3d-series metals, there is only a very small energy difference between the two states, leading to the possibility of spin crossover complexes. Such complexes change their spin state in response to an external stimulus (such as heat or pressure), which in turn leads to a change in their bulk magnetic properties. An example is the $d^6$ iron complex of two diphenylterpyridine ligands (11), which is low-spin ($S = 0$) below 300 K, but high-spin ($S = 2$) above 323 K. The transition from one spin state to another can be abrupt, gradual, or even stepped (Fig 20.42). In the solid state, a further feature of spin crossover complexes is the existence of cooperativity between the magnetic centres, which can lead to hysteresis like that shown in Fig. 20.43.

A preference normally exists for the low-spin state under high pressure and low temperature. This preference can be understood on the basis that the $e_g$ orbitals, which are more extensively occupied in the high-spin state, have significant metal—ligand antibonding character. Thus the high-spin form occupies a larger volume, which is favoured by low pressure or high temperature.

Spin crossover complexes occur in many geological systems, are implicated in the binding of $O_2$ to haemoglobin, and have the potential to be exploited in both practical magnetic information storage and pressure-sensitive devices.

FURTHER READING


The standard reference text on atomic spectra.

EXERCISES

20.1 Determine the configuration (in the form \(t^2\) or \(e^2\)), as appropriate, the number of unpaired electrons, and the ligand-field stabilization energy in terms of \(\Delta_{\pi}\) or \(\Delta_{\sigma}\) and \(P\) for each of the following complexes using the spectrochemical series to decide, where relevant, which are likely to be high-spin and which low-spin.
(a) \([\text{Co}(\text{NH}_3)_6]^{3+}\), (b) \([\text{Fe}(\text{OH})_3]^{3+}\), (c) \([\text{Fe}(	ext{CN})_6]^{3+}\), (d) \([\text{Cr}(\text{NH}_3)_6]^{3+}\), (e) \([\text{W}(	ext{CO})_6]^{3+}\), (f) tetrahedral \([\text{FeCl}_4]^{-}\), (g) tetrahedral \([\text{Ni}(\text{CO})_4]^{-}\).

20.2 Both \(\text{H}^+\) and \(\text{P}(\text{C}_6\text{H}_5)_4\) are ligands of similar field strength, high in the spectrochemical series. Recalling that phosphines act as \(\pi\) acceptors, is \(\pi\)-acceptor character required for strong-field behaviour? What orbital factors account for the strength of each ligand?

20.3 Estimate the spin-only contribution to the magnetic moment for each complex in Exercise 20.1.

20.4 Solutions of the complexes \([\text{Co}(\text{NH}_3)_6]^{3+}\), \([\text{Co}(\text{OH})_2]^{3+}\) (both \(\text{O}_2\)) and \([\text{CoCl}_4]^{2-}\) are coloured. One is pink, another is yellow, and the third is blue. Considering the spectrochemical series and the relative magnitudes of \(\Delta_{\pi}\) and \(\Delta_{\sigma}\) assign each colour to one of the complexes.

20.5 For each of the following pairs of complexes, identify the one that has the larger LFSE:
(a) \([\text{Cr}(\text{OH})_2]^{3+}\) or \([\text{Mn}(\text{OH})_2]^{3+}\)
(b) \([\text{Mn}(\text{OH})_2]^{3+}\) or \([\text{Fe}(\text{OH})_2]^{3+}\)
(c) \([\text{Fe}(\text{OH})_2]^{3+}\) or \([\text{Fe}(	ext{CN})_6]^{3+}\)
(d) \([\text{Fe}(	ext{CN})_6]^{3+}\) or \([\text{Ru}(	ext{CN})_6]^{3+}\)
(e) tetrahedral \([\text{FeCl}_4]^{-}\) or tetrahedral \([\text{CoCl}_4]^{-}\)

20.6 Interpret the variation, including the overall trend across the 3d series, of the following values of oxide lattice enthalpies (in kJ mole\(^{-1}\)). All the compounds have the rock-salt structure: CaO (3460), TiO (3878), VO (3913), MnO (3810), FeO (3921), CoO (3988), NiO (4071).

20.7 A neutral macroyclic ligand with four donor atoms produces a red diamagnetic low-spin d\(^4\) complex of Ni(II) if the anion is the weakly coordinating perchlorate ion. When perchlorate is replaced by two thiocyanate ions, SCN\(^-\), the complex turns violet and is high-spin with two unpaired electrons. Interpret the change in terms of structure.

20.8 Bearing in mind the Jahn–Teller theorem, predict the structure of \([\text{Cr}(\text{OH})_2]^{3+}\).

20.9 The spectrum of d\(^4\) Ti\(^{3+}\)(aq) is attributed to a single electronic transition \(\varepsilon_{1g} \leftarrow t_{2g}\). The band shown in Fig. 20.3 is not symmetrical and suggests that more than one state is involved. Suggest how to explain this observation using the Jahn–Teller theorem.

20.10 Write the Russell–Saunders term symbols for states with the angular momentum quantum numbers \((L, S)\): (a) \((0, \frac{1}{2})\), (b) \((3, \frac{3}{2})\), (c) \((2, \frac{1}{2})\), (d) \((1, 1)\).

20.11 Identify the ground term from each set of terms: (a) \(1\), \(2\), \(3\), \(4\), \(5\), (b) \(P\), \(D\), \(H\), \(I\), \(G\), (c) \(S\), \(P\), \(G\), \(\lambda\)

20.12 Give the Russell–Saunders terms of the configurations: (a) \(4s^1\), \(3p^3\)

20.13 The gas-phase ion V\(^{3+}\) has a \(3\) ground term. The \(1\)D and \(3\)P terms lie, respectively, 10 642 and 12 920 cm\(^{-1}\) above it. The energies of the terms are given in terms of Racah parameters as \(E(\Pi) = A - 8B\), \(E(\Sigma) = A + 7B\), \(E(\Pi) = A - 3B + 2C\). Calculate the values of \(B\) and \(C\) for V\(^{3+}\).

20.14 Write the d-orbital configurations and use the Tanabe–Sugano diagrams (Resource section 6) to identify the ground term of (a) low-spin \([\text{Rh}(\text{NH}_3)_5]^\text{2+}\), (b) \([\text{Ti}(\text{OH})_3]^\text{2+}\), (c) high-spin \([\text{Fe}(\text{OH})_2]^\text{2+}\).

20.15 Using the Tanabe–Sugano diagrams in Resource section 6, estimate \(\Delta_\sigma\) and \(B\) for (a) \([\text{Ni}(\text{OH})_6]^\text{2+}\) (absorptions at 8500, 15 400, and 26 000 cm\(^{-1}\)) and (b) \([\text{Ni}(\text{NH}_3)_6]^\text{2+}\) (absorptions at 10 750, 17 500, and 28 200 cm\(^{-1}\)).

20.16 The spectrum of \([\text{Co}(\text{NH}_3)_6]^{3+}\) has a very weak band in the red and two moderate intensity bands in the visible to near-UV. How should these transitions be assigned?

20.17 Explain why \([\text{FeCl}_3]^\text{2-}\) is colourless whereas \([\text{CoF}_3]^\text{2-}\) is coloured but exhibits only a single band in the visible region of the spectrum.

20.18 The Racah parameter \(B\) is 460 cm\(^{-1}\) in \([\text{Co}(\text{CN})_6]^{3+}\) and 615 cm\(^{-1}\) in \([\text{Ni}(\text{CN})_6]^{2+}\). Consider the nature of bonding with the two ligands and explain the difference in nephelauxetic effect.

20.19 An approximately ‘octahedral’ complex of Co(III) with ammine and chloro ligands gives two bands with \(\varepsilon_{\text{max}}\) between 60 and 80 dm\(^3\) mol\(^{-1}\) cm\(^{-1}\), one weak peak with \(\varepsilon_{\text{max}} = 2\) dm\(^3\) mol\(^{-1}\) cm\(^{-1}\), and a strong band at higher energy with \(\varepsilon_{\text{max}} = 2 \times 10^4\) dm\(^3\) mol\(^{-1}\) cm\(^{-1}\). What do you suggest for the origins of these transitions?

20.20 Ordinary bottle glass appears nearly colourless when viewed through the wall of the bottle but green when viewed from the end so that the light has a long path through the glass. The colour is associated with the presence of Fe\(^{3+}\) in the silicate matrix. Suggest which transitions are responsible for the colour.

20.21 Solutions of \([\text{Cr}(\text{OH})_2]^{3+}\) ions are pale blue—green but the chromate ion, \([\text{CrO}_4]^{2-}\), is an intense yellow. Characterize the origins of the transitions and explain the relative intensities.

20.22 Classify the symmetry type of the d orbitals in a tetragonal \(\text{Cs}\) symmetry complex, such as \([\text{CoCl}(\text{NH}_3)_5]^\text{2+}\), where the Cl\(^-\) lies on the z-axis. (a) Which orbitals will be displaced from their position in the octahedral molecular orbital diagram by \(\pi\) interactions with the lone pairs of the Cl\(^-\) ligand? (b) Which orbital will move because the Cl\(^-\) ligand is not as strong a σ base as NH\(_3\)? (c) Sketch the qualitative molecular orbital diagram for the \(\text{Cs}\) complex.

20.23 Consider the molecular orbital diagram for a tetrahedral complex (based on Fig. 20.8) and the relevant d-orbital configuration and show that the purple colour of MnO\(_4\) cannot arise from a ligand-field transition. Given that the wavenumbers of the two transitions in MnO\(_4\) are 18 500 and 32 200 cm\(^{-1}\), explain how to estimate \(\Delta_\Pi\) from an assignment of the two charge-transfer transitions, even though \(\Delta_\Pi\) cannot be observed directly.

20.24 The lowest energy band in the spectrum of \([\text{Fe}(\text{OH})_2]^{3+}\) (in 1M HClO\(_4\)) occurs at lower energy than the equivalent transition in the spectrum of \([\text{Mn}(\text{OH})_2]^{3+}\). Explain why this is.

PROBLEMS

20.1 In a fused magma liquid from which silicate minerals crystallize, the metal ions can be four-coordinate. In olivine crystals, the M(II) coordination sites are octahedral. Partition coefficients, which are defined as \(K = [\text{M(II)}]_{\text{wall}}/[\text{M(II)}]_{\text{liquid}}\), follow the order Ni(II) > Co(II) > Fe(II) > Mn(II). Account for this in terms of ligand-field theory. (See I.M. Dale and P. Henderson, 24th Int. Geol. Congress, Sect. 1972, 10, 105.)
In Problem 7.11 we looked at the successive formation constants for ethylenediamine complexes of three different metals. Using the same data, discuss the effect of the metal on the formation constant. How might the Irving–Williams series provide insight into these formation constants?

By considering the splitting of the octahedral orbitals as the symmetry is lowered, draw the symmetry-adapted linear combinations and the molecular orbital energy level diagram for σ bonding in a trans-[ML₂X₂] complex. Assume that the ligand X is lower in the spectrochemical series than L.

By referring to Resource section 5, draw the appropriate symmetry-adapted linear combinations and the molecular orbital diagram for π bonding in a square-planar complex. The point group is D₅h. Take note of the small overlap of the ligand with the d₂ orbital. What is the effect of π bonding?

Figures 20.12 and 20.10 show the relationship between the frontier orbitals of octahedral and square-planar complexes. Construct similar diagrams for two-coordinate linear complexes.

Consider a trigonal prismatic six-coordinate ML₆ complex with D₅h symmetry. Use the D₅h character table to divide the d orbitals of the metal into sets of defined symmetry type. Assume that the ligands are at the same angle relative to the xy-plane as in a tetrahedral complex.

In a trigonal bipyramidal complex ligand the axial and equatorial sites have different steric and electronic interactions with the central metal ion. Consider a range of some common ligands and decide which coordination site in a trigonal bipyramidal complex they would favour. (See A.R. Rossi and R. Hoffmann, Inorg. Chem., 1975, 14, 365.)

Vanadium(IV) species that have the V=O group have quite distinct spectra. What is the d-electron configuration of V(IV)? The most symmetrical of such complexes are VOL with C₃v symmetry with the O atom on the z-axis. What are the symmetry species of the five d orbitals in VOL complexes? How many d–d bands are expected in the spectra of these complexes? A band near 24 000 cm⁻¹ in these complexes shows vibrational progressions of the V=O vibration, implicating an orbital involving V=O bonding. Which d–d transition is a candidate? (See C.J. Ballhausen and H.B. Gray, Inorg. Chem., 1962, 1, 111.)

The compound Ph₃Sn–Re(CO)₅(Bu-DAB) (Bu-DAB = ‘Bu−N=CH=N−Bu) has a metal-to-diimine ligand MLCT band as the lowest energy transition in its spectrum. Irradiation of this band gives an Re(CO)₅(Bu-DAB) radical as a photochemical product. The EPR spectrum shows extensive hyperfine splitting by ¹⁴N and ¹⁹F. The radical is assigned as a complex of the DAB radical anion with Re(I). Explain the argument (see D.J. Stufkens, Coord. Chem. Rev., 1990, 104, 39).

MLCT bands can be recognized by the fact that the energy is a sensitive function of the polarity of the solvent (because the excited state is more polar than the ground state). Two simplified molecular orbital diagrams are shown in Fig. 20.44. In (a) is a case with a ligand π level higher than the metal d orbital. In (b) is a case in which the metal d orbital and the ligand level are at the same energy. Which of the two MLCT bands should be more solvent sensitive? These two cases are realized by [W(CO)₅(phen)] and [W(CO)₅(Pr-DAB)], where DAB = 1,4-diaza-1,3-butadiene, respectively. (See P.C. Servas, H.K. van Dijk, T.L. Snoeck, D.J. Stufkens, and A. Oskam, Inorg. Chem., 1985, 24, 4494.) Comment on the CT character of the transition as a function of the extent of back-donation by the metal atom.

Figure 20.44 Representation of the orbitals involved in MLCT transitions for cases in which the energy of the ligand π* orbital varies with respect to the energy of the metal d orbital. See Problem 20.10.

Consider spin crossover complexes and identify the features that a complex would need for it to be used in (a) a practical pressure sensor and (b) a practical information storage device (see P. Gütlich, Y. Garcia, and H.A. Goodwin, Chem. Soc. Rev., 2000, 29, 419).
Coordination chemistry: reactions of complexes

We now look at the evidence and experiments that are used in the analysis of the reaction pathways of metal complexes and so develop a deeper understanding of their mechanisms. Because a mechanism is rarely known definitively, the nature of the evidence for it should always be kept in mind in order to recognize that there might be other consistent possibilities. In the first part of this chapter we consider ligand exchange reactions and describe how reaction mechanisms are classified. We consider the steps by which the reactions take place and the details of the formation of the transition state. These concepts are then used to describe the mechanisms of the redox reactions of complexes.

Coordination chemistry is not the sole preserve of d metals. Whereas Chapter 20 dealt exclusively with d metals, this chapter builds on the introduction to coordination chemistry in Chapter 7 and applies it to all metals regardless of the block to which they belong. However, there are special features of each block, and we shall point them out.

**Ligand substitution reactions**

The most fundamental reaction a complex can undergo is ligand substitution, a reaction in which one Lewis base displaces another from a Lewis acid:

\[ Y + M \rightarrow X \rightarrow M + Y \]

This class of reaction includes complex formation reactions, in which the leaving group, the displaced base \( X \), is a solvent molecule and the entering group, the displacing base \( Y \), is some other ligand. An example is the replacement of a water ligand by Cl⁻:

\[ [\text{Co(OH}_2]_6^{2+} + \text{Cl}^- \rightarrow [\text{CoCl(OH}_2]_5^{3+} + \text{H}_2\text{O}] \]

The thermodynamic aspects of complex formation are discussed in Sections 7.12 to 7.15.

21.1 Rates of ligand substitution

**Key points:** The rates of substitution reactions span a very wide range and correlate with the structures of the complexes; complexes that react quickly are called labile, those that react slowly are called inert or nonlabile.

Rates of reaction are as important as equilibria in coordination chemistry. The numerous isomers of the ammines of Co(III) and Pt(II), which were so important to the development of the subject, could not have been isolated if ligand substitutions and interconversion of the isomers had been fast. But what determines whether one complex will survive for long periods whereas another will undergo rapid reaction?

The rate at which one complex converts into another is governed by the height of the activation energy barrier that lies between them. Thermodynamically unstable complexes that survive for long periods (by convention, at least a minute) are commonly called ‘inert’, but nonlabile is more appropriate and is the term we shall use. Complexes that undergo more rapid equilibration are called labile. An example of each type is the labile complex \([\text{Ni(OH}_2]_6^{2+}\) \], which has a half-life of the order of milliseconds before the \( \text{H}_2\text{O} \) is replaced.
by another \( \text{H}_2\text{O} \) or a stronger base, and the nonlabile complex \([\text{Co(NH}_3\text{)}_5\text{(OH}_2\text{)}]^{3+}\), in which \( \text{H}_2\text{O} \) survives for several minutes as a ligand before it is replaced by a stronger base.

Figure 21.1 shows the characteristic lifetimes of the important aqua metal ion complexes. We see a range of lifetimes starting at about 1 ns, which is approximately the time it takes for a molecule to diffuse one molecular diameter in solution. At the other end of the scale are lifetimes in years. Even so, the illustration does not show the longest times that could be considered, which are comparable to geological eras.

We shall examine the lability of complexes in greater detail when we discuss the mechanism of reactions later in this section, but we can make two broad generalizations now. The first is that complexes of metals that have no additional factor to provide extra stability (for instance, the LFSE and chelate effects) are among the most labile. Any additional stability of a complex results in an increase in activation energy for a ligand replacement reaction and hence decreases the lability of the complex. A second generalization is that very small ions are often less labile because they have greater \( M\text{T}_{\text{H}} \) bond strengths and it is sterically very difficult for incoming ligands to approach the metal atom closely.

Some further generalizations are as follows:

1. All complexes of s-block ions except the smallest (\( \text{Be}^{2+} \) and \( \text{Mg}^{2+} \)) are very labile.
2. Complexes of the M(III) ions of the f block are all very labile.
3. Complexes of the \( d^{10} \) ions (\( \text{Zn}^{2+} \), \( \text{Cd}^{2+} \), and \( \text{Hg}^{2+} \)) are normally very labile.
4. Across the 3d series, complexes of d-block M(II) ions are generally moderately labile, with distorted Cu(II) complexes among the most labile.
5. Complexes of d-block M(III) ions are distinctly less labile than d-block M(II) ions.
6. d-Metal complexes with \( d^1 \) and low-spin \( d^0 \) configurations (for example Cr(III), Fe(II), and Co(III)) are generally nonlabile as they have large LFSEs. Chelate complexes with the same configuration, such as \([\text{Fe(phen)}]^{2+}\), are particularly inert.
7. Nonlability is common among the complexes of the 4d and 5d series, which reflects the high LFSE and strength of the metal—ligand bonding.

Table 21.1 illustrates the range of timescales for a number of reactions.

The natures of the ligands in the complex also affect the rates of reactions. The identity of the incoming ligand has the greatest effect, and equilibrium constants of displacement reactions can be used to rank ligands in order of their strength as Lewis bases. However, a different order may be found if bases are ranked according to the rates at which they displace a ligand from the central metal ion. Therefore, for kinetic considerations, we replace the equilibrium concept of basicity by the kinetic concept of nucleophilicity, the rate of attack on a complex by a given Lewis base relative to the rate of attack by a reference Lewis base. The shift from equilibrium to kinetic considerations is emphasized by referring to ligand displacement as nucleophilic substitution.

Ligands other than the entering and leaving groups may play a significant role in controlling the rates of reactions; these ligands are referred to as spectator ligands.
Ligand substitution reactions

For instance, it is observed for square-planar complexes that the ligand trans to the leaving group X has a great effect on the rate of substitution of X by the entering group Y.

21.2 The classification of mechanisms

The mechanism of a reaction is the sequence of elementary steps by which the reaction takes place. Once the mechanism has been identified, attention turns to the details of the activation process of the rate-determining step. In some cases the overall mechanism is not fully resolved, and the only information available is the rate-determining step.

(a) Association, dissociation, and interchange

Key points: The mechanism of a nucleophilic substitution reaction is the sequence of elementary steps by which the reaction takes place and is classified as associative, dissociative, or interchange; an associative mechanism is distinguished from an interchange mechanism by demonstrating that the intermediate has a relatively long life.

The first stage in the kinetic analysis of a reaction is to study how its rate changes as the concentrations of reactants are varied. This type of investigation leads to the identification of rate laws, the differential equations governing the rate of change of the concentrations of reactants and products. For example, the observation that the rate of formation of $[\text{Ni(NH}_3\text{)}_2\text{OH}_3]^{2+}$ from $[\text{Ni(OH}_2\text{)}_6]^{2+}$ is proportional to the concentration of both $\text{NH}_3$ and $[\text{Ni(OH}_2\text{)}_6]^{2+}$ implies that the reaction is first order in each of these two reactants, and that the overall rate law is:

$$\text{rate} = k_r[Ni(OH)_2^{2+}][NH_3] \quad (21.1)$$

A note on good practice In rate equations, as in expressions for equilibrium constants, we omit the brackets that are part of the chemical formula of the complex; the surviving brackets denote molar concentration. We denote rate constants by $k_r$ to avoid possible confusion with Boltzmann's constant.

In simple sequential reaction schemes, the slowest elementary step of the reaction dominates the overall reaction rate and the overall rate law, and is called the rate-determining step. However, in general, all the steps in the reaction may contribute to the rate law and affect its rate. Therefore, in conjunction with stereochemical and isotopic labelling studies, the determination of the rate law is the route to the elucidation of the mechanism of the reaction.

Three main classes of reaction mechanism have been identified. A dissociative mechanism, denoted $D_s$, is a reaction sequence in which an intermediate of reduced coordination number is formed by the departure of the leaving group:

$$\text{ML}_nX \rightarrow \text{ML}_n^+ + X$$
$$\text{ML}_n^+ + Y \rightarrow \text{ML}_nY$$
Here MLₙ (the metal atom and any spectator ligands) is a true intermediate that can, in principle, be detected (or even isolated). The typical form of the corresponding reaction profile is shown in Fig. 21.2.

- **A brief illustration.** The substitution of hexacarbonyltungsten by phosphine takes place by dissociation of CO from the complex

\[ W(CO)_6 \rightarrow W(CO)_5 + CO \]

followed by coordination of phosphine:

\[ W(CO)_5 + PPh₃ \rightarrow W(CO)_5(PPh₃) \]

Under the conditions in which this reaction is usually performed in the laboratory, the intermediate \( W(CO)_5 \) is rapidly captured by the solvent, such as tetrahydrofuran, to form \( [W(CO)_5(thf)] \). This complex in turn is converted to the phosphine product, presumably by a second dissociative process.

An **associative mechanism**, denoted \( A \), involves a step in which an intermediate is formed with a higher coordination number than the original complex:

\[ MLₙX + Y \rightarrow MLₙXY \]

\[ MLₙXY \rightarrow MLₙX + Y \]

Once again, the intermediate \( MLₙXY \) can, in principle, at least, be detected. This mechanism plays a role in many reactions of square-planar Au(III), Pt(II), Pd(II), Ni(II), and Ir(I) \( d⁶ \) complexes. The typical form of the reaction profile is similar to that of the dissociative mechanism, and is shown in Fig. 21.3.

- **A brief illustration.** The first step in the exchange of \( ^{14}CN^{-} \) with the ligands in the square-planar complex \( [Ni(CN)]^{3-} \) is the coordination of a ligand to the complex:

\[ [Ni(CN)]^{3-} + ^{14}CN^{-} \rightarrow [Ni(CN)_{(14)CN}]^{3-} \]

A ligand is then discarded:

\[ [Ni(CN)_{(14)CN}]^{3-} \rightarrow [Ni(CN)]^{3-} + CN^{-} \]

The radioactivity of carbon-14 provides a means of monitoring this reaction, and the intermediate \( [Ni(CN)]^{3-} \) has been detected and isolated.

An **interchange mechanism**, denoted \( I \), takes place in one step:

\[ MLₙX + Y \rightarrow X \cdots MLₙ \cdots Y \rightarrow MLₙY + X \]

The leaving and entering groups exchange in a single step by forming a transition state but not a true intermediate. The interchange mechanism is common for many reactions of six-coordinate complexes. The typical form of the reaction profile is shown in Fig. 21.4.

The distinction between the \( A \) and \( I \) mechanisms hinges on whether or not the intermediate persists long enough to be detectable. One type of evidence is the isolation of an intermediate in another related reaction or under different conditions. If an argument by extrapolation to the actual reaction conditions suggests that a moderately long-lived intermediate might exist during the reaction in question, then the \( A \) path is indicated. For example, the synthesis of the first trigonal-bipyramidal Pt(II) complex, \( [Pt(SnCl₂)]^{3-} \), indicates that a five-coordinate platinum complex may be plausible in substitution reactions of square-planar Pt(II) ammine complexes. Similarly, the fact that \( [Ni(CN)]^{3-} \) is observed spectroscopically in solution, and that it has been isolated in the crystalline state, provides support for the view that it is involved when \( CN^{-} \) exchanges with the square-planar tetracyanidonickelate(II) ion.

A second indication of the persistence of an intermediate is the observation of a stereochemical change, which implies that the intermediate has lived long enough to undergo rearrangement. *Cis* to *trans* isomerization is observed in the substitution reactions of certain square-planar phosphine Pt(II) complexes, which is in contrast to the retention of configuration usually observed. This difference implies that the trigonal-bipyramidal intermediate lives long enough for an exchange between the axial and equatorial ligand positions to occur.
Direct spectroscopic detection of the intermediate, and hence an indication of A rather than I, may be possible if a sufficient amount accumulates. Such direct evidence, however, requires an unusually stable intermediate with favourable spectroscopic characteristics.

(b) The rate-determining step

**Key point:** The rate-determining step is classified as associative or dissociative according to the dependence of its rate on the identity of the entering group.

Now we consider the rate-determining step of a reaction and the details of its formation. The step is called associative and denoted a if its rate depends strongly on the identity of the incoming group. Examples are found among reactions of the d^9 square-planar complexes of Pt(II), Pd(II), and Au(III), including

\[ [PtCl(dien)]^+(aq) + I^-(aq) \rightarrow [PtI(dien)]^+(aq) + Cl^-(aq) \]

where dien is diethylentriamine (NH\(_2\)CH\(_2\)CH\(_2\)NHCH\(_2\)CH\(_2\)NH\(_2\)). It is found, for instance, that use of I\(^-\) instead of Br\(^-\) increases the rate constant by an order of magnitude. Experimental observations on the substitution reactions of square-planar complexes support the view that the rate-determining step is associative.

The strong dependence of the rate-determining step on entering group Y indicates that the transition state must involve significant bonding to Y. A reaction with an associative mechanism (A) will be associatively activated (a) if the attachment of Y to the initial reactant ML\(_X\) is the rate-determining step; such a reaction is designated A\(_a\), and in this case the intermediate ML\(_X Y\) would not be detected. A reaction with a dissociative mechanism (D) is dissociatively activated (d) if the attachment of Y to the intermediate ML\(_X\) is the rate-determining step; such a reaction is designated D\(_d\). Figure 21.5 shows the reaction profiles for associatively activated A and D mechanisms. For the reactions to proceed, it is necessary to have established a population of an encounter complex X–M, Y in a pre-equilibrium step.

The rate-determining step is called **dissociative** and denoted d if its rate is largely independent of the identity of Y. This category includes some of the classic examples of ligand substitution in octahedral d-metal complexes, including

\[ [Ni(OH\(_2\))_2]^+(aq) + NH_3(aq) \rightarrow [Ni(NH\(_3\))(OH\(_2\))_2]^+(aq) + H_2O(l) \]

It is found that replacement of NH\(_3\) by pyridine in this reaction changes the rate by at most a few per cent.

The weak dependence on Y of a dissociatively activated process indicates that the rate of formation of the transition state is determined largely by the rate at which the bond to the leaving group X can break. A reaction with an associative mechanism (A) will be dissociatively activated (d) if the loss of X from the intermediate YML\(_X\) is the rate-determining step; such a reaction is designated A\(_d\). A reaction with a dissociative mechanism (D) is dissociatively activated (d) if the initial loss of X from the reactant ML\(_X\) is the rate-determining step, such a reaction is designated D\(_d\). In this case, the intermediate ML\(_X\) would not be detected. Figure 21.6 shows the reaction profiles for dissociatively activated A and D mechanisms.

A reaction that has an interchange mechanism (I) can be either associatively or dissociatively activated, and is designated either I\(_a\) or I\(_d\), respectively. In an I\(_a\) mechanism, the rate of reaction depends on the rate at which the M–Y bond forms, whereas in an I\(_d\) reaction the rate of reaction depends on the rate at which the M–X bond breaks (Fig. 21.7).

The distinction between these possibilities may be summarized as follows, where ML\(_X\) denotes the initial complex:

<table>
<thead>
<tr>
<th>Mechanism:</th>
<th>( A )</th>
<th>( I )</th>
<th>( D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation:</td>
<td>( a )</td>
<td>( d )</td>
<td>( a )</td>
</tr>
<tr>
<td>Rate- determining step</td>
<td>Y attaching to ML(_X)</td>
<td>Loss of X from ( \text{ML}_X )</td>
<td>Y attaching to ML(_X)</td>
</tr>
<tr>
<td>Detect intermediate?</td>
<td>no</td>
<td>( \text{ML}_XY ) detectable</td>
<td>no</td>
</tr>
</tbody>
</table>

**Figure 21.5** The typical form of the reaction profile of reactions with an associatively activated step: (a) associative mechanism, A\(_a\); (b) a dissociative mechanism, D\(_d\).
Ligand substitution in square-planar complexes

The mechanism of ligand exchange in square-planar Pt complexes has been studied extensively, largely because the reactions occur on a timescale that is very amenable to investigation. We might expect an associative mechanism of ligand exchange because square-planar complexes are sterically uncrowded—they can be considered as octahedral complexes with two ligands missing—but it is rarely that simple. The elucidation of the mechanism of the substitution of square-planar complexes is often complicated by the occurrence of alternative pathways. For instance, if a reaction such as

\[
[\text{PtCl(dien)}]^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow [\text{PtI(dien)}]^+(\text{aq}) + \text{Cl}^-(\text{aq})
\]

is first order in the complex and independent of the concentration of \( \text{I}^- \), then the rate of reaction will be equal to \( k_r,1[\text{PtCl(dien)}]^+ \). However, if there is a pathway in which the rate law is first order in the complex and first order in the incoming group (that is, overall second order) then the rate would be given by \( k_r,2[\text{PtCl(dien)}]^+][\text{I}^-] \). If both reaction pathways occur at comparable rates, the rate law has the form

\[
\text{rate} = (k_{r,1} + k_{r,2})[\text{I}^-][\text{PtCl(dien)}]^+ \tag{21.2}
\]

A reaction like this is usually studied under the conditions \([\text{I}^-] >> [\text{complex}]\) so that \([\text{I}^-]\) does not change significantly during the reaction. This simplifies the treatment of the data as \( k_{r,1} + k_{r,2}[\text{I}^-] \) is effectively constant and the rate law is now pseudo-first order:

\[
\text{rate} = k_{r,obs}[\text{PtCl(dien)}]^+ \quad k_{r,obs} = k_{r,1} + k_{r,2}[\text{I}^-] \tag{21.3}
\]

A plot of the observed pseudo-first-order rate constant against \([\text{I}^-]\) gives \( k_{r,2} \) as the slope and \( k_{r,1} \) as the intercept.
In the following sections, we examine the factors that affect the second-order reaction and then consider the first-order process.

21.3 The nucleophilicity of the entering group

Key points: The nucleophilicity of an entering group is expressed in terms of the nucleophilicity parameter defined in terms of the substitution reactions of a specific square-planar platinum complex; the sensitivity of other platinum complexes to changes in the entering group is expressed in terms of the nucleophilic discrimination factor.

We start by considering the variation of the rate of the reaction as the entering group Y is varied. The reactivity of Y (for instance, I⁻ in the reaction above) can be expressed in terms of a nucleophilicity parameter, $n_n$:

$$ n_n = \log \frac{k_r(Y)}{k_o} \tag{21.4} $$

where $k_r(Y)$ is the second-order rate constant for the reaction

$$ \text{trans-[PtCl}_2\text{(py)}_2] + Y \rightarrow \text{trans-[PtClY(py)}_2] + \text{Cl}^- $$

and $k_o$ is the rate constant for the same reaction with the reference nucleophile methanol. The entering group is highly nucleophilic, or has a high nucleophilicity, if $n_n$ is large.

Table 21.2 gives some values of $n_n$. One striking feature of the data is that, although the entering groups in the table are all quite simple, the rate constants span nearly nine orders of magnitude. Another feature is that the nucleophilicity of the entering group towards Pt appears to correlate with soft Lewis basicity (Section 4.12), with Cl⁻ < I⁻, O < S, and NH₃ < PR₃.

The nucleophilicity parameter is defined in terms of the reaction rates of a specific platinum complex. When the complex itself is varied we find that the reaction rates show a range of different sensitivities towards changes in the entering group. To express this range of sensitivities we rearrange eqn 21.4 into

$$ \log k_r(Y) = n_n(Y) + C \tag{21.5} $$

where $C = \log k_o$. Now consider the analogous substitution reactions for the general complex [PtL₂X]:

$$ [\text{PtL}_2X] + Y \rightarrow [\text{PtL}_2Y] + X $$

The relative rates of these reactions can be expressed in terms of the nucleophilicity parameter $n_n$ provided we replace eqn 21.5 by

$$ \log k_r(Y) = S n_n(Y) + C \tag{21.6} $$

The parameter S, which characterizes the sensitivity of the rate constant to the nucleophilicity parameter, is called the nucleophilic discrimination factor. We see that the straight line obtained by plotting $\log k_r(Y)$ against $n_n$ for reactions of Y with $\text{trans-[PtCl}_2\text{(py)}_2]$, the red circles in Fig. 21.8, is steeper than that for reactions with $\text{cis-[PtCl}_2\text{(en)}]$, the blue squares in Fig. 21.8. Hence, S is larger for the former reaction, which indicates that the rate of the reaction is more sensitive to changes in the nucleophilicity of the entering group.

Some values of S are given in Table 21.3. Note that S is close to 1 in all cases, so all the complexes are quite sensitive to $n_n$. This sensitivity is what we expect for associatively activated reactions. Another feature to note is that larger values of S are found for complexes of platinum with softer base ligands.

**EXAMPLE 21.1 Using the nucleophilicity parameter**

The second-order rate constant for the reaction of I⁻ with $\text{trans-[Pt(CH}_3\text{)Cl(P}\text{Et}_3]}$ in methanol at 30°C is 40 dm³ mol⁻¹ s⁻¹. The corresponding reaction with $\text{N}_3^-$ has $k_r = 7.0$ dm³ mol⁻¹ s⁻¹. Estimate S and C for the reaction given the $n_n$ values of 5.42 and 3.58, respectively, for the two nucleophiles.
The spectator ligands $T$ that are detected.

Almost invariably has an associative rate-determining stage; hence intermediates are rarely shed light on the general shape of the transition state. They also confirm that substitution almost invariably has an associative rate-determining stage; hence intermediates are rarely detected.

(a) The $\textit{trans}$ effect

**Key point:** A strong $\sigma$-donor ligand or $\pi$-acceptor ligand greatly accelerates substitution of a ligand that lies in the $\textit{trans}$ position.

The spectator ligands $T$ that are $\textit{trans}$ to the leaving group in square-planar complexes influence the rate of substitution. This phenomenon is called the $\textit{trans}$ effect. It is generally accepted that the $\textit{trans}$ effect arises from two separate influences: one arising in the ground state and the other in the transition state itself.

The $\textit{trans}$ influence is the extent to which the ligand $T$ weakens the bond $\textit{trans}$ to itself in the ground state of the complex. The $\textit{trans}$ influence correlates with the $\sigma$-donor ability of the ligand $T$ because, broadly speaking, ligands $\textit{trans}$ to each other use the same orbitals on the metal for bonding. Thus if one ligand is a strong $\sigma$ donor, then the ligand $\textit{trans}$ to it cannot donate electrons to the metal so well, and thus has a weaker interaction with the metal. The $\textit{trans}$ influence is assessed quantitatively by measuring bond lengths, stretching frequencies, and metal-to-ligand NMR coupling constants (Section 8.5). The $\textit{transition state}$ effect correlates with the $\pi$-acceptor ability of the ligand. Its origin is thought to be the increase in electron density on the metal atom arising due to the incoming ligand: any ligand that can accept this increased electron density will stabilize the transition state (1). The $\textit{trans}$ effect is the combination of both effects; it should be noted that the same factors contribute to a large ligand-field splitting. $\textit{Trans}$ effects are listed in Table 21.4 and follow the order:

For a $T\sigma$-donor: $\text{OH}^- < \text{NH}_3 < \text{Cl}^- < \text{Br}^- < \text{CN}^-; \text{CH}_3^- < \text{I}^- < \text{SCN}^- < \text{PR}_3, \text{H}^-$

For a $T\pi$-acceptor: $\text{Br}^- < \text{I}^- < \text{NCS}^- < \text{NO}_2^- < \text{CN}^- < \text{CO}, \text{C}_2\text{H}_4$

**Table 21.3** Nucleophilic discrimination factors

<table>
<thead>
<tr>
<th>$S$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[PtCl(PEt)$_3$]</td>
<td>1.43</td>
</tr>
<tr>
<td>trans-[PtCl(py)$_3$]</td>
<td>1.00</td>
</tr>
<tr>
<td>[PtCl(en)]</td>
<td>0.64</td>
</tr>
<tr>
<td>trans-[PtCl(dien)]$^+$</td>
<td>0.65</td>
</tr>
</tbody>
</table>

**Answer** To determine $S$ and $C$, we need to use the two pieces of information to set up and solve two simultaneous equations based on eqn 21.6. Substituting the two values of $n_i$ into eqn 21.6 gives:

$$1.60 = 5.42S + C \quad (\text{for } I^-)$$

$$0.85 = 3.58S + C \quad (\text{for } \text{N}_3^-)$$

Solving these two simultaneous equations gives $S = 0.41$ and $C = -0.62$. The value of $S$ is fairly small, showing that the discrimination of this complex among different nucleophiles is not great. This lack of sensitivity is related to the fairly large value of $C$, which corresponds to the rate constant being large and hence to the complex being reactive. It is commonly found that high reactivity correlates with low selectivity.

**Self-test 21.1** Calculate the second-order rate constant for the reaction of the same complex with NO$_2^-$, for which $n_i = 3.22$.

**Example 21.2** Using the $\textit{trans}$ effect synthetically

Use the $\textit{trans}$ effect series to suggest synthetic routes to $\textit{cis}$- and $\textit{trans}$-[PtCl$_3$(NH$_3$)$_3$] from [Pt(NH$_3$)$_4$]$^{2+}$ and [PtCl$_3$]$^{2-}$.

**Answer** If we consider the reaction of [Pt(NH$_3$)$_4$]$^{2+}$ with HCl we can see it leads to [PtCl(NH$_3$)$_3$]$^+$, now, because the $\textit{trans}$ effect of Cl$^-$ is greater than that of NH$_3$, substitution reactions will occur preferentially $\textit{trans}$ to Cl$^-$, and further action of HCl gives $\textit{trans}$-[PtCl$_3$(NH$_3$)$_3$] $^+$:

$$[\text{Pt(NH}_3)_4]^2+ + \text{Cl}^- \rightarrow [\text{PtCl(NH}_3)_3]^+ \rightarrow \text{trans-[PtCl}_3(\text{NH}_3)_3]^+$$

21.4 The shape of the transition state

Careful studies of the variation of the reaction rates of square-planar complexes with changes in the composition of the reactant complex and the conditions of the reaction shed light on the general shape of the transition state. They also confirm that substitution almost invariably has an associative rate-determining stage; hence intermediates are rarely detected.

**Example 21.2** Using the $\textit{trans}$ effect synthetically

Use the $\textit{trans}$ effect series to suggest synthetic routes to $\textit{cis}$- and $\textit{trans}$-[PtCl$_3$(NH$_3$)$_3$] from [Pt(NH$_3$)$_4$]$^{2+}$ and [PtCl$_3$]$^{2-}$.

**Answer** If we consider the reaction of [Pt(NH$_3$)$_4$]$^{2+}$ with HCl we can see it leads to [PtCl(NH$_3$)$_3$]$^+$, now, because the $\textit{trans}$ effect of Cl$^-$ is greater than that of NH$_3$, substitution reactions will occur preferentially $\textit{trans}$ to Cl$^-$, and further action of HCl gives $\textit{trans}$-[PtCl$_3$(NH$_3$)$_3$] $^+$:

$$[\text{Pt(NH}_3)_4]^2+ + \text{Cl}^- \rightarrow [\text{PtCl(NH}_3)_3]^+ \rightarrow \text{trans-[PtCl}_3(\text{NH}_3)_3]^+$$
However, when the starting complex is \([\text{PtCl}_4]^{2-}\), reaction with \(\text{NH}_3\) leads first to \([\text{PtCl}_4(\text{NH}_3)]^{-}\). A second step should substitute one of the two mutually \textit{trans} \(\text{Cl}^{-}\) ligands with \(\text{NH}_3\) to give \textit{cis}\{-\text{PtCl}_4(\text{NH}_3)\}.

\[
\text{[PtCl}_4]^{2-} + \text{NH}_3 \rightarrow \text{[PtCl}_4(\text{NH}_3)]^{-} \rightarrow \text{cis-}[\text{PtCl}_4(\text{NH}_3)]
\]

**Self-test 21.2** Given the reactants \(\text{PPh}_3\), \(\text{NH}_3\), and \([\text{PtCl}_4]^{2-}\), propose efficient routes to both \textit{cis-} and \textit{trans-} \([\text{PtCl}_4(\text{NH}_3)(\text{PPh}_3)]\).

**(b) Steric effects**

**Key point:** Steric crowding at the reaction centre usually inhibits associative reactions and facilitates dissociative reactions.

Steric crowding at the reaction centre by bulky groups that can block the approach of attacking nucleophiles will inhibit associative reactions. The rate constants for the replacement of \(\text{Cl}^{-}\) by \(\text{H}_2\text{O}\) in \textit{cis-}[\text{PtCl}(\text{PEt}_3)]\ complexes at 25°C illustrate the point:

\[
\begin{align*}
\text{L} & \quad \text{pyridine} \quad \text{2-methylpyridine} \quad \text{2,6-dimethylpyridine} \\
\text{k/s}^{-1} & \quad 8 \times 10^{-2} \quad 2.0 \times 10^{-4} \quad 1.0 \times 10^{-6}
\end{align*}
\]

The methyl groups adjacent to the N donor atom greatly decrease the rate. In the 2-methylpyridine complex they block positions either above or below the plane. In the 2,6-dimethylpyridine complex they block positions both above and below the plane (2). Thus, along the series, the methyl groups increasingly hinder attack by \(\text{H}_2\text{O}\).

The effect is smaller if \(\text{L}\) is \textit{trans} to \(\text{Cl}^{-}\). This difference is explained by the methyl groups then being further from the entering and leaving groups in the trigonal-bipyramidal transition state if the pyridine ligand is in the trigonal plane (3). Conversely, the decrease in coordination number that occurs in a dissociative reaction can relieve the steric overcrowding and thus increase the rate of the dissociative reaction.

**(c) Stereochemistry**

**Key point:** Substitution of a square-planar complex preserves the original geometry, which suggests a trigonal-pyramidal transition state.

Further insight into the nature of the transition state is obtained from the observation that substitution of a square-planar complex preserves the original geometry. That is, a \textit{cis} complex gives a \textit{cis} product and a \textit{trans} complex gives a \textit{trans} product. This behaviour is explained by the formation of an approximately trigonal-bipyramidal transition state with the entering, leaving, and \textit{trans} groups in the trigonal plane (4).\(^1\) Trigonal-bipyramidal intermediates of this type account for the relatively small influence that the two \textit{cis} spectator ligands have on the rate of substitution, as their bonding orbitals will be largely unaffected by the course of the reaction.

The steric course of the reaction is shown in Fig. 21.9. We can expect a \textit{cis} ligand to exchange places with the T ligand in the trigonal plane only if the intermediate lives long enough to be stereomobile. That is, it must be a long-lived associative (A) intermediate, with release of the ligand from the five-coordinate intermediate being the rate-determining step.

**(d) Temperature and pressure dependence**

**Key point:** Negative volumes and entropies of activation support the view that the rate-determining step of square-planar Pt(II) complexes is associative.

Another clue to the nature of the transition state comes from the entropies and volumes of activation for reactions of Pt(II) and Au(III) complexes (Table 21.5). The entropy of activation is obtained from the temperature dependence of the rate constant, and indicates the change in disorder (of reactants and solvent) when the transition state forms. Likewise, the volume of activation, which is obtained (with considerable difficulty) from the pressure dependence of the rate constant, is the change in volume that occurs on formation of the transition state.

\(^1\) Note that the stereochemistry is quite different from that of p-block central atoms, such as Si(IV) and P(V), where the leaving group departs from the more crowded axial position.
(e) The first-order pathway

**Key point:** The first-order contribution to the rate law is a pseudo-first-order process in which the solvent participates.

Having considered factors that affect the second-order pathway, we can now consider the first-order pathway for the substitution of square-planar complexes. The first issue we must address is the first-order pathway in the rate equation and decide whether $k_{i,1}$ in the rate law in eqn 21.2 and its generalization

$$\text{rate} = (k_{i,1} + k_{i,2}[Y]) [\text{PtL}_4]$$

(21.7)

does indeed represent the operation of an entirely different reaction mechanism. It turns out that it does not, and $k_{i,1}$ represents an associative reaction involving the solvent. In this pathway the substitution of $\text{Cl}^-$ by pyridine in methanol as solvent proceeds in two steps, with the first rate-determining:

$$[\text{PtCl(dien)}]^+ + \text{CH}_3\text{OH} \rightarrow [\text{Pt}($\text{CH}_3\text{OH}$)(dien)]^{2+} + \text{Cl}^- \quad \text{(slow)}$$

$$[\text{Pt}($\text{CH}_3\text{OH}$)(dien)]^{2+} + \text{py} \rightarrow [\text{Pt}($\text{py}$)(dien)]^{2+} + \text{CH}_3\text{OH} \quad \text{(fast)}$$

The evidence for this two-step mechanism comes from a correlation of the rates of these reactions with the nucleophilicity parameters of the solvent molecules and the observation that reactions of entering groups with solvent complexes are rapid when compared to the

---

**Table 21.5 Activation parameters for substitution in square-planar complexes (in methanol)**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_{i,1}$</th>
<th>$k_{i,2}$</th>
<th>$\Delta^H$</th>
<th>$\Delta^S$</th>
<th>$\Delta^V$</th>
<th>$\Delta^H$</th>
<th>$\Delta^S$</th>
<th>$\Delta^V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-$[\text{PtCl(NO}_2\text{)(py)}_2] + \text{py}$</td>
<td>50</td>
<td>-100</td>
<td>-38</td>
<td>71</td>
<td>-84</td>
<td>-46</td>
<td>46</td>
<td>-138</td>
</tr>
<tr>
<td>trans-$[\text{PtBrP}_2\text{mes}] + \text{SC(NH}_2\text{)}_2$</td>
<td>84</td>
<td>-59</td>
<td>-67</td>
<td>63</td>
<td>-121</td>
<td>-63</td>
<td>79</td>
<td>-71</td>
</tr>
<tr>
<td>cis-$[\text{PtBrP}_2\text{mes}] + \text{I}^-$</td>
<td>79</td>
<td>-71</td>
<td>-71</td>
<td>54</td>
<td>-17</td>
<td>54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-$[\text{PtBrP}_2\text{mes}] + \text{SC(NH}_2\text{)}_2$</td>
<td>71</td>
<td>-84</td>
<td>-46</td>
<td>46</td>
<td>-138</td>
<td>-54</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>$[\text{AuCl(dien)}]^+ + \text{Br}^-$</td>
<td>79</td>
<td>-71</td>
<td>-71</td>
<td>59</td>
<td>-121</td>
<td>-54</td>
<td>54</td>
<td>-17</td>
</tr>
</tbody>
</table>

[PtBrP$_2$(mes)] is [PtBr(PEt$_3$)$_2$(2,4,6-Me$_3$C$_6$H$_2$)].

Enthalpy in kilojoules per mole (kJ mol$^{-1}$); entropy in J K$^{-1}$ mol$^{-1}$ and volume in cm$^3$ mol$^{-1}$.

---

The limiting cases for the volume of activation in ligand substitution reactions correspond to the increase in molar volume of the outgoing ligand (for a dissociative reaction) and the decrease in molar volume of the incoming ligand (for an associative reaction).

The two striking aspects of the data in the table are the consistently strongly negative values of both quantities. The simplest explanation of the decrease in disorder and the decrease in volume is that the entering ligand is being incorporated into the transition state without release of the leaving group. That is, we can conclude that the rate-determining step is associative.

---

**Figure 21.9** The stereochemistry of substitution in a square-planar complex. The normal path (resulting in retention) is from (a) to (c). However, if intermediate (b) is sufficiently long-lived, it can undergo pseudorotation to (d), which leads to isomer (e).
step in which the solvent displaces a ligand. Thus, the substitution of ligands at a square-planar platinum complex results from two competing associative reactions.

**Ligand substitution in octahedral complexes**

Octahedral complexes occur for a wide variety of metals in a wide range of oxidation states and with a great diversity of bonding modes. We might therefore expect a wide variety of mechanisms of substitution; however, almost all octahedral complexes react by the interchange mechanism. The only real question is whether the rate-determining step is associative or dissociative. The analysis of rate laws for reactions that take place by such a mechanism helps to formulate the precise conditions for distinguishing these two possibilities and identifying the substitution as \( I_a \) (interchange with an associative rate-determining stage) or \( I_d \) (interchange with a dissociative rate-determining stage). The difference between the two classes of reaction hinges on whether the rate-determining step is the formation of the new \( Y \cdots M \) bond or the breaking of the old \( M \cdots X \) bond.

21.5 **Rate laws and their interpretation**

Rate laws provide an insight into the detailed mechanism of a reaction in the sense that any proposed mechanism must be consistent with the observed rate law. In the following section we see how the rate laws found experimentally for ligand substitution are interpreted.

(a) The Eigen—Wilkins mechanism

**Key points:** In the Eigen—Wilkins mechanism, an encounter complex is formed in a pre-equilibrium step and the encounter complex forms products in a subsequent rate-determining step.

As an example of a ligand substitution reaction, we consider

\[
[Ni(OH_2)_6]^{2+} + NH_3 \rightarrow [Ni(NH_3)(OH_2)_5]^{2+} + H_2O
\]

The first step in the Eigen—Wilkins mechanism is an encounter in which the complex \( ML_6 \), in this case \( [Ni(OH_2)_6]^{2+} \), and the entering group \( Y \), in this case \( NH_3 \), diffuse together and come into contact:

\[
[Ni(OH_2)_6]^{2+} + NH_3 \rightarrow [[Ni(OH_2)_5]^{2+},NH_3]
\]

The two components of the encounter pair, the entity \( \{A,B\} \), may also separate at a rate governed by their ability to migrate by diffusion through the solvent:

\[
[[Ni(OH_2)_5]^{2+},NH_3] \rightarrow [Ni(OH_2)_6]^{2+} + NH_3
\]

Because in aqueous solution the lifetime of an encounter pair is approximately 1 ns, the formation of the pair can be treated as a pre-equilibrium in all reactions that take longer than a few nanoseconds. Consequently, we can express the concentrations in terms of a pre-equilibrium constant \( K_E \):

\[
ML_6 + Y \rightleftharpoons \{ML_6,Y\} \quad \quad K_E = \frac{[\{ML_6,Y\}]}{[ML_6][Y]}
\]

The second step in the mechanism is the rate-determining reaction of the encounter complex to give products:

\[
[[Ni(OH_2)_5]^{2+},NH_3] \rightarrow [Ni(NH_3)(OH_2)_5]^{2+} + H_2O
\]

and in general

\[
[ML_6,Y] \rightarrow ML_5Y + L \quad \quad \text{rate} = k_r[[ML_6,Y]]
\]

We cannot simply substitute \([ML_6,Y] = K_E[ML_6][Y]\) into this expression because the concentration of \( ML_6 \) must take into account the fact that some of it is present as the encounter pair; that is, \([M]_{tot} = [ML_6,Y] + [ML_6]_i\), the total concentration of the complex. It follows that

\[
\text{rate} = \frac{k_r K_E [M]_{tot} [Y]}{1 + K_E [Y]} \tag{21.8}
\]
It is rarely possible to conduct experiments over a range of concentrations wide enough to test eqn 21.8 exhaustively. However, at such low concentrations of the entering group that \( K_\text{eq}[Y] \ll 1 \), the rate law reduces to

\[
\text{rate} = k_{\text{obs}}[M][Y] \quad k_{\text{obs}} = k_e K_e \quad (21.9)
\]

Because \( k_{\text{obs}} \) can be measured and \( K_e \) can be either measured or estimated as we describe below, the rate constant \( k_e \) can be found from \( k_{\text{obs}}/K_e \). The results for reactions of Ni(II) hexaaqua complexes with various nucleophiles are shown in Table 21.6. The very small variation in \( k_e \) indicates a model \( k_e \) reaction with very slight sensitivity to the nucleophilicity of the entering group.

When \( Y \) is a solvent molecule the encounter equilibrium is ‘saturated’ in the sense that, because the complex is always surrounded by solvent, a solvent molecule is always available to take the place of one that leaves the complex. In such a case \( K_e[Y] \gg 1 \) and \( k_{\text{obs}} = k_e \).

Thus, reactions with the solvent can be directly compared to reactions with other entering ligands without needing to estimate the value of \( K_e \).

(b) The Fuoss–Eigen equation

**Key point:** The Fuoss–Eigen equation provides an estimate of the pre-equilibrium constant based on the strength of the Coulombic interaction between the reactants and their distance of closest approach.

The equilibrium constant \( K_e \) for the encounter pair can be estimated by using a simple equation proposed independently by R.M. Fuoss and M. Eigen. Both sought to take the complex size and charge into account, expecting larger, oppositely charged ions to meet more frequently than small ions of the same charge. Fuoss used an approach based on statistical thermodynamics and Eigen used one based on kinetics. Their result, which is called the **Fuoss–Eigen equation**, is

\[
K_e = \frac{A}{a} \frac{z_1 z_2}{V} N_A e^{-V/kT} \quad (21.10)
\]

In this expression \( a \) is the distance of closest approach of ions of charge numbers \( z_1 \) and \( z_2 \) in a medium of permittivity \( \varepsilon \), \( V \) is the Coulombic potential energy \( (z_1 z_2 e^2/4\pi \varepsilon a) \) of the ions at that distance, and \( N_A \) is Avogadro’s constant. Although the value predicted by this equation depends strongly on the details of the charges and radii of the ions, typically it clearly favours the encounter if the reactants are large (so \( a \) is large) or oppositely charged (\( V \) negative).

**A brief illustration.** If one of the reactants is uncharged (as in the case of substitution by \( \text{NH}_3 \)), then \( V = 0 \) and \( K_e = \frac{A}{a} \frac{z_2}{V} N_A \). For an encounter distance of 200 pm for neutral species, we find

\[
K_e = \frac{4\pi}{3} \times (2.00 \times 10^{-10} \text{ m})^3 \times (6.022 \times 10^{23} \text{ mol}^{-1}) = 2.02 \times 10^{-3} \text{ m}^{-1} \text{ mol}^{-1}
\]

or \( 2.02 \times 10^{-2} \text{ dm}^{-3} \text{ mol}^{-1} \). For two singly charged ions of opposite charge in water at 298 K (when \( \varepsilon_r = 78 \)), other factors being equal, the value of \( K_e \) is increased by a factor of

\[
e^{-V/kT} = e^{2\varepsilon A \pi a} akT = 36
\]

Table 21.6 Complex formation by the \([\text{Ni(OH)}_6]^{3+}\) ion

<table>
<thead>
<tr>
<th>Ligand</th>
<th>( k_{\text{obs}}/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) )</th>
<th>( K_e/(\text{dm}^3 \text{ mol}^{-1}) )</th>
<th>( (k_{\text{obs}}/K_e) \text{Y/s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{CO}_2^- )</td>
<td>1 \times 10^4</td>
<td>3</td>
<td>3 \times 10^4</td>
</tr>
<tr>
<td>( \text{F}^- )</td>
<td>8 \times 10^4</td>
<td>1</td>
<td>8 \times 10^4</td>
</tr>
<tr>
<td>( \text{HF} )</td>
<td>3 \times 10^4</td>
<td>0.15</td>
<td>2 \times 10^4</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}^* )</td>
<td>3 \times 10^4</td>
<td>3 \times 10^4</td>
<td></td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
<td>5 \times 10^4</td>
<td>0.15</td>
<td>3 \times 10^4</td>
</tr>
<tr>
<td>([\text{NH}_3\text{CH}_2\text{NH}_3]^- )</td>
<td>4 \times 10^4</td>
<td>0.02</td>
<td>2 \times 10^4</td>
</tr>
<tr>
<td>( \text{SCN}^- )</td>
<td>6 \times 10^4</td>
<td>1</td>
<td>6 \times 10^4</td>
</tr>
</tbody>
</table>

* The solvent is always in encounter with the ion so that \( K_e \) is undefined and all rates are inherently first order.
21.6 The activation of octahedral complexes

Many studies of substitution in octahedral complexes support the view that the rate-determining step is dissociative, and we summarize these studies first. However, the reactions of octahedral complexes can acquire a distinct associative character in the case of large central ions (as in the 4d and 5d series) or where the d-electron population at the metal is low (the early members of the d block). More room for attack or lower π* electron density appears to facilitate nucleophilic attack and hence permit association.

(a) Leaving-group effects

**Key points:** A large effect of the leaving group X is expected in \( I_p \) reactions; a linear relation is found between the logarithms of the rate constants and equilibrium constants.

We can expect the identity of the leaving group X to have a large effect in dissociatively activated reactions because their rates depend on the scission of the M–X bond. When X is the only variable, as in the reaction

\[
[\text{CoX(NH}_3)_5]^2+ + \text{H}_2\text{O} \rightarrow [\text{Co(NH}_3)_5(\text{OH}_2)]^2+ + \text{X}^- 
\]

it is found that the rate constant and equilibrium constant of the reaction are related by

\[
\ln k = \ln K + c \quad (21.11)
\]

This correlation is illustrated in Fig. 21.10. Because both logarithms are proportional to Gibbs energies (ln \( k_p \) is approximately proportional to the activation Gibbs energy, \( \Delta^r G \)), and ln K is proportional to the standard reaction Gibbs energy, \( \Delta G^o \), we can write the following linear free energy relation (LFER):

\[
\Delta^r G = p\Delta G^o + b \quad (21.12)
\]

with p and b constants (and \( p = 1 \)).

The existence of an LFER of unit slope, as for the reaction of \([\text{CoX(NH}_3)_5]^2+\), shows that changing X has the same effect on \( \Delta^r G \) for the conversion of Co–X to the transition state as it has on \( \Delta G^o \) for the complete elimination of X (Fig. 21.11). This observation in turn suggests that in a reaction with an interchange mechanism and a dissociative rate-determining step (\( I_p \)), the leaving group (an anionic ligand) has already become a solvated ion in the transition state. An LFER with a slope of less than 1, indicating some associative character, is observed for the corresponding complexes of Rh(III). For Co(III), the reaction rates are in the order \( I^- > Br^- > Cl^- \) whereas for Rh(III) they are reversed, and are in the order \( I^- < Br^- < Cl^- \). This difference should be expected as the softer Rh(III) centre forms more stable complexes with \( I^- \), compared with \( Br^- \) and \( Cl^- \), whereas the harder Co(III) centre forms more stable complexes with \( Cl^- \).

(b) The effects of spectator ligands

**Key points:** In octahedral complexes, spectator ligands affect rates of substitution; the effect is related to the strength of the metal–ligand interaction, with stronger donor ligands increasing the reaction rate by stabilizing the transition state.

In Co(III), Cr(III), and related octahedral complexes, both cis and trans ligands affect rates of substitution in proportion to the strength of the bonds they form with the metal atom. For instance, hydrolysis reactions such as

\[
[\text{NiL}_5]^+ + \text{H}_2\text{O} \rightarrow [\text{NiL}_5(\text{OH})_2] + \text{X}^- 
\]

are much faster when L is NH\(_3\) than when it is H\(_2\)O. This difference can be explained on the grounds that, as NH\(_3\) is a stronger σ donor than H\(_2\)O, it increases the electron density at the metal atom and hence facilitates the scission of the M–X bond and the formation of X\(^-\). In the transition state, the stronger donor stabilizes the reduced coordination number.

(c) Steric effects

**Key point:** Steric crowding favours dissociative activation because formation of the transition state can relieve strain.

Steric effects on reactions with dissociative rate-determining steps can be illustrated by considering the rate of hydrolysis of the first Cl\(^-\) ligand in two complexes of the type \([\text{CoCl}_3(\text{bn})_2]^+\):

\[
[\text{CoCl}_3(\text{bn})_2]^+ + \text{H}_2\text{O} \rightarrow [\text{CoCl(OH})(\text{bn})_2]^2+ + \text{Cl}^- 
\]

**Figure 21.10** The straight line obtained when the logarithm of a rate constant is plotted against the logarithm of an equilibrium constant shows the existence of a linear free energy relation. The graph is for the reaction \([\text{Co(NH}_3)_5X]^2+ + \text{H}_2\text{O} \rightarrow [\text{Co(NH}_3)_5(\text{OH})_2]^2+ + \text{X}^-\) with different leaving groups X.

**Figure 21.11** The existence of a linear free energy relation with unit slope shows that changing X has the same effect on \( \Delta^r G \) for the conversion of M–X to the transition state as it has on \( \Delta G^o \) for the complete elimination of X\(^-\). The reaction profile shows the effect of changing the leaving group from X to X\(^-'\).
The ligand \( \text{bn} \) is 2,3-butanediamine, and may be either chiral (5) or achiral (6). The important observation is that the complex formed with the chiral form of the ligand hydrolyses 30 times more slowly than the complex of the achiral form. The two ligands have very similar electronic effects, but the \( \text{CH}_3 \) groups are on the opposite sides of the chelate ring in (5) but adjacent and crowded in (6). The latter arrangement is more reactive because the strain is relieved in the dissociative transition state with its lowered coordination number.

In general, steric crowding favours an \( I_d \) process because the five-coordinate transition state can relieve strain.

Quantitative treatments of the steric effects of ligands have been developed using molecular modelling computer software that takes into account van der Waals interactions. However, a more pictorial semiquantitative approach was introduced by C.A. Tolman. In this approach, the extent to which various ligands (especially phosphines) crowd each other is assessed by approximating the ligand by a cone with an angle determined from a space-filling model and, for phosphine ligands, an M–P bond length of 228 pm (Fig. 21.12 and Table 21.7). The ligand CO is small in the sense of having a small cone angle; \( \text{P(t-Bu)}_3 \) is regarded as bulky because it has a large cone angle. Bulky ligands have considerable steric repulsion with each other when packed around a metal centre. They favour dissociative activation and inhibit associative activation.

As an illustration, the rate of the reaction of \([\text{Ru(CO)}_3(\text{PR}_3)(\text{SiCl}_3)]_2\) (7) with \( Y \) to give \([\text{Ru(CO)}_2Y(\text{PR}_3)(\text{SiCl}_3)]_2\) is independent of the identity of \( Y \), which suggests that the rate-determining step is dissociative. Furthermore, it has been found that there is only a small variation in rate for the substituents \( Y \) with similar cone angles but significantly different values of \( \text{pK}_a \). This observation supports the assignment of the rate changes to steric effects because changes in \( \text{pK}_a \) should correlate with changes in electron distributions in the ligands.

(d) Activation energetics

**Key point:** A significant loss of LFSE on going from the starting complex to the transition state results in nonlabile complexes.

One factor that has a strong bearing on the activation of complexes is the difference between ligand field stabilization energy (LFSE, Section 20.1) of the reacting complex and that of the transition state (the LFSE). This difference is known as the ligand field activation energy (LFAE):

\[
\text{LFAE} = \text{LFSE}^{\text{‡}} - \text{LFSE}^{\text{Δ}}
\]

Table 21.8 gives calculated values of LFAE for the replacement of \( \text{H}_2\text{O} \) at a hexaaqua ion, assuming a square-pyramidal transition state (that is, a dissociatively activated reaction), and shows there is correlation between a large \( \Delta H \) and a large LFAE. Thus, we can begin to see why \( \text{Ni}^{2+} \) and \( \text{V}^{2+} \) complexes are not very labile: they have large activation energies which arise, in part, from a significant loss of LFSE on moving from an octahedral complex to a transition state.

**Table 21.7** Tolman cone angles for various ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>( \theta/° )</th>
<th>Ligand</th>
<th>( \theta/° )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3 )</td>
<td>90</td>
<td>( \text{P(OC}_6\text{H}_5)_3 )</td>
<td>127</td>
</tr>
<tr>
<td>CO</td>
<td>95</td>
<td>( \text{PBu}_3 )</td>
<td>130</td>
</tr>
<tr>
<td>( \text{Cl, Et} )</td>
<td>102</td>
<td>( \text{PEt}_3 )</td>
<td>132</td>
</tr>
<tr>
<td>( \text{PF}_3 )</td>
<td>104</td>
<td>( \eta^5\text{C}_5\text{H}_5(\text{Cp}) )</td>
<td>136</td>
</tr>
<tr>
<td>( \text{Br, Ph} )</td>
<td>105</td>
<td>( \text{PPh}_3 )</td>
<td>145</td>
</tr>
<tr>
<td>( \text{I, P(OCH}_3)_3 )</td>
<td>107</td>
<td>( \eta^5\text{C}_5\text{Me}_5(\text{Cp}^*) )</td>
<td>165</td>
</tr>
<tr>
<td>( \text{PMe}_3 )</td>
<td>118</td>
<td>2,4\text{Me}_2\text{C}_5\text{H}_3</td>
<td>180</td>
</tr>
<tr>
<td>( \text{t-Butyl} )</td>
<td>126</td>
<td>( \text{P(t-Bu)}_3 )</td>
<td>182</td>
</tr>
</tbody>
</table>

\(^2\) Tolman’s studies were on nickel complexes, so strictly speaking we are talking about a Ni–P distance of 228 pm.
Activation parameters for the $\text{H}_2\text{O}$ exchange reactions

$$[\text{M(OH}_2)_6]^{3+} + \text{H}_2\text{O} \rightarrow [\text{M(OH}_2)\text{OH}_2]^{3+} + \text{H}_2\text{O}$$

<table>
<thead>
<tr>
<th></th>
<th>$\Delta^iH^\circ$ (kJ mol$^{-1}$)</th>
<th>LFSE$^*/\Delta_o$</th>
<th>(LFSE)$^*/\Delta_o$</th>
<th>LFAE/$\Delta_o$</th>
<th>$\Delta^iV$ (cm$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{3+}$ (d$^2$)</td>
<td>0.8</td>
<td>0.91</td>
<td>-0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V$^{3+}$ (d$^4$)</td>
<td>68.6</td>
<td>1.2</td>
<td>1</td>
<td>0.2</td>
<td>-4.1</td>
</tr>
<tr>
<td>Cr$^{3+}$ (d$^4$, hs)</td>
<td>0.6</td>
<td>0.91</td>
<td>-0.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn$^{2+}$ (d$^5$, hs)</td>
<td>33.9</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$^{3+}$ (d$^6$, hs)</td>
<td>31.2</td>
<td>0.4</td>
<td>0.46</td>
<td>-0.06</td>
<td>+3.8</td>
</tr>
<tr>
<td>Co$^{3+}$ (d$^7$, hs)</td>
<td>43.5</td>
<td>0.8</td>
<td>0.91</td>
<td>-0.11</td>
<td>+6.1</td>
</tr>
<tr>
<td>Ni$^{2+}$ (d$^8$)</td>
<td>58.1</td>
<td>1.2</td>
<td>1</td>
<td>0.2</td>
<td>+7.2</td>
</tr>
</tbody>
</table>

* Octahedral. † Square pyramidal. hs, high spin.

(e) Associative activation

**Key point:** A negative volume of activation indicates association of the entering group into the transition state.

As we have seen, the activation volume reflects the change in compactness (including that of the surrounding solvent) when the transition state forms from the reactants. The last column in Table 21.8 gives $\Delta^iV$ for some $\text{H}_2\text{O}$ ligand-exchange reactions. We see that $\Delta^iV$ becomes more positive, from $-4.1$ cm$^3$ mol$^{-1}$ for V$^{3+}$ to $+7.2$ cm$^3$ mol$^{-1}$ for Ni$^{2+}$. Because a negative volume of activation can be interpreted as the result of shrinkage when an $\text{H}_2\text{O}$ molecule becomes part of the transition state, we can infer that the activation has significant associative character. The increase in $\Delta^iV$ follows the increase in the number of nonbonding d electrons from d$^1$ to d$^8$ across the 3d series. In the earlier part of the d block, associative reaction appears to be favoured by a low population of d electrons.

Negative volumes of activation are also observed in the 4d and 5d series, such as for Rh(III), and indicate an associative interaction of the entering group in the transition state of the reaction. Associative activation begins to dominate when the metal centre is more accessible to nucleophilic attack, either because it is large or has a low (nonbonding or $\pi^*$) d-electron population, and the mechanism shifts from $I_1$ towards $I_2$. Table 21.9 shows some data for the formation of Br$^-$, Cl$^-$, and NCS$^-$ complexes from $[\text{Cr(NH}_3)_3\text{OH}_2]^+$ and $[\text{Cr(OH}_2)_3\text{Cl}]^{3+}$. In contrast to the strong dependence of the hexaaqua complex, the pentammine complex shows only a weak dependence on the identity of the nucleophile. The two complexes probably mark a transition from $I_1$ to $I_2$. In addition, the rate constants for the replacement of $\text{H}_2\text{O}$ in $[\text{Cr(OH}_2)_3\text{Cl}]^{3+}$ by Cl$^-$, Br$^-$, or NCS$^-$ are smaller by a factor of about 10$^4$ than those for the analogous reactions of $[\text{Cr(NH}_3)_3\text{OH}_2]^+$.

This difference suggests that the NH$_3$ ligands, which are stronger donors than $\text{H}_2\text{O}$, promote dissociation of the sixth ligand more effectively. As we saw above, this behaviour is to be expected in dissociatively activated reactions.

**Table 21.9** Kinetic parameters for anion attack on Cr(III)*

<table>
<thead>
<tr>
<th>$X^-$</th>
<th>$k$ (10$^{-8}$ dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>$L = \text{H}_2\text{O}$</th>
<th>$\Delta^iH^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta^iS^\circ$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>$L = \text{NH}_3$</th>
<th>$k$ (10$^{-4}$ dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br$^-$</td>
<td>0.46</td>
<td>122</td>
<td>8</td>
<td>3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1.15</td>
<td>126</td>
<td>38</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCS$^-$</td>
<td>48.7</td>
<td>105</td>
<td>4</td>
<td>4.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Reaction is $[\text{CrL}_3\text{OH}_2]^+$ + $X^-$ $\rightarrow$ $[\text{CrL}_3\text{Cl}]^{3+}$ + $\text{H}_2\text{O}$

*The limiting value for $\Delta^iV$ is approximately ±18 cm$^3$ mol$^{-1}$, the molar volume of water, with $A$ reactions having negative and $D$ reactions positive values.
EXAMPLE 21.3 Interpreting kinetic data in terms of a mechanism

The second-order rate constants for formation of [VX(OH)$_3$]$_2$$^+$ from [V(OH)$_2$]$_3$$^+$ and X$^-$ for X$^-$ = Cl$^-$, NCS$^-$, and NO$_3^-$ are in the ratio 1.2:10. What do the data suggest about the rate-determining step for the substitution reaction?

**Answer** We need to consider the factors that might affect the rate of the reaction. All three ligands are singly charged anions of similar size, so we can expect the encounter equilibrium constants to be similar. Therefore, the second-order rate constants are proportional to first-order rate constants for substitution in the encounter complex. The second-order rate constant is equal to $K_k$, where $K$ is the pre-equilibrium constant and $k_r$ is the first-order rate constant for substitution of the encounter complex. The greater rate constants for NCS$^-$ than for Cl$^-$, and especially the five-fold difference of NCS$^-$ from its close structural analogue N$_3^-$, suggest some contribution from nucleophilic attack and an associative reaction. By contrast, there is no such systematic pattern for the same anions reacting with Ni(II), for which the reaction is believed to be dissociative.

**Selftest 21.3** Use the data in Table 21.8 to estimate an appropriate value for $K_k$ and calculate $k_r$ for the reactions of V(II) with Cl$^-$ if the observed second-order rate constant is $1.2 \times 10^2$ dm$^3$ mol$^{-1}$ s$^{-1}$.

21.7 Base hydrolysis

**Key points:** Octahedral substitution can be greatly accelerated by OH$^-$ ions when ligands with acidic hydrogens are present as a result of the decrease in charge of the reactive species and the increased ability of the deprotonated ligand to stabilize the transition state.

Consider a substitution reaction in which the ligands possess acidic protons, such as

$$[\text{CoCl(NH}_3)_2]^{2+} + \text{OH}^- \rightarrow [\text{Co(OH)(NH}_3)_2]^{2+} + \text{Cl}^-$$

An extended series of studies has shown that whereas the rate law is overall second order, with rate $= k_J[\text{CoCl(NH}_3)_2]^{2+}[\text{OH}^-]$, the mechanism is not a simple bimolecular attack by OH$^-$ on the complex. For instance, whereas the replacement of Cl$^-$ by OH$^-$ is fast, the replacement of Cl$^-$ by F$^-$ is slow, even though F$^-$ resembles OH$^-$ more closely in terms of size and nucleophilicity. There is a considerable body of indirect evidence relating to the problem but one elegant experiment makes the essential point. This conclusive evidence comes from a study of the $^{18}$O/$^{16}$O isotope distribution in the product $[\text{Co(OH)(NH}_3)_2]^{2+}$. It is known that the $^{18}$O/$^{16}$O ratio differs between H$_2$O and OH$^-$ at equilibrium, and this fact can be used to establish whether the incoming group is H$_2$O or OH$^-$. The $^{18}$O/$^{16}$O isotope ratio in the cobalt product matches that for H$_2$O, not that for the OH$^-$ ions, proving that it is an H$_2$O molecule that is the entering group.

The mechanism that takes these observations into account supposes that the role of OH$^-$ is to act as a Brønsted base, not an entering group:

$$[\text{CoCl(NH}_3)_2]^{2+} + \text{OH}^- \rightarrow [\text{CoCl(NH}_3(H)_2]^{2+} + \text{H}_2\text{O}$$

$$[\text{CoCl(NH}_3(H)_2]^{2+} \rightarrow [\text{Co(NH}_3)_2]^{2+} + \text{Cl}^- \text{ (slow)}$$

$$[\text{Co(NH}_3)_2]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Co(OH)(NH}_3)_2]^{2+} \text{ (fast)}$$

In the first step, an NH$_3$ ligand acts as a Brønsted acid, resulting in the formation of its conjugate base, the NH$_2^-$ ion, as a ligand. Because the deprotonated form of the complex has a lower charge, it will be able to lose a Cl$^-$ ion more readily than the protonated form, thus accelerating the reaction. In addition, according to the conjugate base mechanism, loss of a proton from an NH$_3$ ligand changes it from a pure σ-donor ligand to a strong σ and π donor (as NH$_2^-$) and so helps to stabilize the five-coordinate transition state, greatly accelerating the loss of the Cl$^-$ ion (see the next brief illustration).

21.8 Stereochemistry

**Key point:** Reaction through a square-pyramidal intermediate results in retention of the original geometry but reaction through a trigonal-bipyramidal intermediate can lead to isomerization.

Classic examples of octahedral substitution stereochemistry are provided by Co(III) complexes. Table 21.10 shows some data for the hydrolysis of cis- and trans-[CoAX(en)$_3$]$^{2+}$

<table>
<thead>
<tr>
<th>A</th>
<th>X</th>
<th>Percentage cis in product</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis</td>
<td>OH$^-$</td>
<td>100</td>
</tr>
<tr>
<td>cis</td>
<td>Cl$^-$</td>
<td>100</td>
</tr>
<tr>
<td>cis</td>
<td>NCS$^-$</td>
<td>100</td>
</tr>
<tr>
<td>cis</td>
<td>NO$_3^-$</td>
<td>0</td>
</tr>
<tr>
<td>trans</td>
<td>Cl$^-$</td>
<td>50–70</td>
</tr>
<tr>
<td>trans</td>
<td>NCS$^-$</td>
<td>35</td>
</tr>
<tr>
<td>trans</td>
<td>OH$^-$</td>
<td>75</td>
</tr>
</tbody>
</table>

X is the leaving group.
Ligand substitution in octahedral complexes

(8) and (9), respectively, where X is the leaving group (either Cl\(^-\) or Br\(^-\)) and A is OH\(^-\), NCS\(^-\), or Cl\(^-\). The stereochemical consequences of substitution of octahedral complexes are much more intricate than those of square-planar complexes. The cis complexes do not undergo isomerization when substitution occurs, whereas the trans forms show a tendency to isomerize in the order A = NO\(_2^+\) < Cl\(^-\) < NCS\(^-\) < OH\(^-\).

The data can be understood in terms of an I\(_d\) mechanism and by recognizing that the five-coordinate metal centre in the transition state may resemble either of the two stable geometries for five-coordination, namely square-pyramidal or trigonal-bipyramidal. As can be seen from Fig. 21.13, reaction through the square-pyramidal complex results in retention of the original geometry but reaction through the trigonal-bipyramidal complex can lead to isomerization. The cis complex gives rise to a square-pyramidal intermediate but the trans isomer gives a trigonal-bipyramidal intermediate. For d metals, trigonal-bipyramidal complexes are favoured when the ligands in the equatorial positions are good π donors, and a good π-donor ligand trans to the leaving group Cl\(^-\) favours isomerization (10).

A brief illustration. Substitution of Co(III) complexes of the type [CoAX(en)]\(^+\) results in trans to cis isomerization, but only when the reaction is catalysed by a base. In a base hydrolysis reaction, one of the NH\(_2\)R groups of the en ligands loses a proton and becomes its conjugate base, \(\text{NHR}^+\). The \(\text{NHR}^+\) ligand group is a strong π-donor ligand and favours a trigonal bipyramid of the type shown in Fig. 21.13 and it may be attacked in the way shown there. If the direction of attack of the incoming ligands were random, we would expect 33 per cent trans and 67 per cent cis product.

21.9 Isomerization reactions

Key points: Isomerization of a complex can take place by mechanisms that involve substitution, bond cleavage, and reformation, or twisting.

Isomerization reactions are closely related to substitution reactions; indeed, a major pathway for isomerization is often via substitution. The square-planar Pt(II) and octahedral Co(III) complexes we have discussed can form five-coordinate trigonal-bipyramidal transition states. The interchange of the axial and equatorial ligands in a trigonal-bipyramidal complex can be pictured as occurring by a Berry pseudorotation through a square-pyramidal conformation (Section 7.4 and Fig. 21.14). As we have seen, when a trigonal-bipyramidal complex adds a ligand to produce a six-coordinate complex, a new direction of attack of the entering group can result in isomerization.

If a chelate ligand is present, isomerization can occur as a consequence of metal—ligand bond breaking, and substitution need not occur. An example is the exchange of the ‘outer’ CD\(_3\) group with the ‘inner’ CH\(_3\) group during the isomerization of a substituted tris(acetylacetonato)cobalt(III) complex, (11) \(\rightarrow\) (12). An octahedral complex can also undergo isomerization by an intramolecular twist without loss of a ligand or breaking of a bond. There is evidence, for example, that racemization of [Ni(en)]\(^{3+}\) occurs by such an internal twist. Two possible paths are the Bailar twist and the Ray–Dutt twist (Fig. 21.15).

![Figure 21.13](image1.png) Reaction through a square-pyramidal complex (top path) results in retention of the original geometry, but reaction through a trigonal-bipyramidal complex (bottom path) can lead to isomerization.

![Figure 21.14](image2.png) The exchange of axial and equatorial ligands by a twist through a square-pyramidal conformation of the complex.
Redox reactions

As remarked in Chapter 5, redox reactions can occur by the direct transfer of electrons (as in some electrochemical cells and in many solution reactions) or by the transfer of atoms and ions, as in the transfer of O atoms in reactions of oxidoanions. Because redox reactions in solution involve both an oxidizing and a reducing agent, they are usually bimolecular in character. The exceptions are reactions in which one molecule has both oxidizing and reducing centres.

21.10 The classification of redox reactions

Key points: In an inner-sphere redox reaction a ligand is shared to form a transition state; in an outer-sphere redox reaction there is no bridging ligand between the reacting species.

In the 1950s, Henry Taube identified two mechanisms of redox reactions for metal complexes. One is the inner-sphere mechanism, which includes atom-transfer processes. In an inner-sphere mechanism, the coordination spheres of the reactants share a ligand transiently and form a bridged transition state. The other is an outer-sphere mechanism, which includes many simple electron transfers. In an outer-sphere mechanism, the complexes come into contact without sharing a bridging ligand and the electron tunnels from one metal atom to the other.

The mechanisms of some redox reactions have been definitively assigned as inner- or outer-sphere. However, the mechanisms of a vast number of reactions are unknown because it is difficult to make unambiguous assignments when complexes are labile. Much of the study of well-defined examples is directed towards the identification of the parameters that differentiate the two paths with the aim of being able to making correct assignments in more difficult cases.

21.11 The inner-sphere mechanism

Key point: The rate-determining step of an inner-sphere redox reaction may be any one of the component processes, but a common one is electron transfer.

The inner-sphere mechanism was first confirmed for the reduction of the nonlabile complex [CoCl(NH$_3$)$_5$]Cl$^+$ by Cr$^{2+}$(aq). The products of the reaction included both Co$^{2+}$(aq) and [CrCl(OH$_2$)$_5$]Cr$^{2+}$, and addition of $^{36}$Cl$^-$ to the solution did not lead to the incorporation of any of the isotope into the Cr(III) product. Furthermore, the reaction is much faster than reactions that remove Cl$^-$ from nonlabile Co(III) or introduce Cl$^-$ into the nonlabile [Cr(OH$_2$)$_5$]Cr$^{2+}$ complex. These observations suggest that Cl$^-$ has moved directly from the coordinating sphere of one complex to that of the other during the reaction. The Cl$^-$ attached to Co(III) can easily enter into the labile coordination sphere of [Cr(OH$_2$)$_5$]Cr$^{2+}$ to produce a bridged intermediate (13).

Inner-sphere reactions, though involving more steps than outer-sphere reactions, can be fast. Figure 21.16 summarizes the steps necessary for such a reaction to occur.
Redox reactions

The first two steps of an inner-sphere reaction are the formation of a precursor complex and the formation of the bridged binuclear intermediate. These two steps are identical to the first two steps in the Eigen–Wilkins mechanism (Section 21.5). The final steps are electron transfer through the bridging ligand to give the successor complex, followed by dissociation to give the products.

The rate-determining step of the overall reaction may be any one of these processes, but the most common one is the electron-transfer step. However, if both metal ions have a nonlabile electron configuration after electron transfer, then the break-up of the bridged complex is rate determining. An example is the reduction of \([\text{RuCl(NH}_3\text{)}_5]^2+\) by \([\text{Cr(OH}_2\text{)}_6]^{2+}\), in which the rate-determining step is the dissociation of the Cl-bridged complex \([\text{Ru}^{II}(\text{NH}_3)_5(\mu-\text{Cl})\text{Cr}^{III}(\text{OH}_2)_6]^{4+}\). Reactions in which the formation of the bridged complex is rate determining tend to have similar rate constants for a series of partners of a given species. For example, the oxidation of \(V^{II}(aq)\) has similar rate constants for a long series of Co(III) oxidants with different bridging ligands. The explanation is that the rate-determining step is the substitution of an H\(_2\)O molecule from the coordination sphere of V(III), which is quite slow (Table 21.8).

Figure 21.16 The different pathways followed by inner- and outer-sphere mechanisms.
The numerous reactions in which electron transfer is rate determining do not display such simple regularities. Rates vary over a wide range as metal ions and bridging ligands are varied. The data in Table 21.11 show some typical variations as bridging ligand, oxidizing metal, and reducing metal are changed.

All the reactions in Table 21.11 result in the change of oxidation number by ±1. Such reactions are still often called one-equivalent processes, the name reflecting the largely outdated term ‘chemical equivalent’. Similarly, reactions that result in the change of oxidation number by ±2 are often called two-equivalent processes and may resemble nucleophilic substitutions. This resemblance can be seen by considering the reaction

\[
[\text{Pt}^{2+}\text{Cl}_5]^2+ + [\text{Pt}^{4+}\text{Cl}_5]^2+ \rightarrow [\text{Pt}^{4+}\text{Cl}_5]^2+ + [\text{Pt}^{2+}\text{Cl}_5]^2+
\]

which occurs through a Cl\(^{-}\) bridge (14). The reaction depends on the transfer of a Cl\(^{-}\) ion in the break-up of the successor complex.

There is no difficulty in assigning an inner-sphere mechanism when the reaction involves ligand transfer from an initially nonlabile reactant to a nonlabile product. With more labile complexes, inner-sphere reactions should always be suspected when ligand transfer occurs as well as electron transfer, and if good bridging groups such as Cl\(^{−}\), Br\(^{−}\), I\(^{−}\), N\(_2\)^{−}, CN\(^{−}\), SCN\(^{−}\), pyrazine (15), 4,4’-bipyridine (16), and 4-dimethylaminopyridine (17) are present. Although all these ligands have lone pairs to form the bridge, this may not be an essential requirement. For instance, just as the carbon atom of a methyl group can act as a bridge between OH\(^{−}\) and I\(^{−}\) in the hydrolysis of iodomethane, so it can act as a bridge between Cr(II) and Co(III) in the reduction of methylcobalt species by Cr(II).

The oxidation of a metal centre by oxidoanions is also an example of an inner-sphere process. For example, in the oxidation of Mo(IV) by NO\(_3^{−}\) ions, an O atom of the nitrate ion binds to the Mo atom, facilitating the electron transfer from Mo to N, and then remains bound to the Mo(VI) product:

\[
\text{Mo(IV)} + \text{NO}_3^{−} \rightarrow \text{Mo}−\text{O}−\text{O} = \text{NO}_2^{−} \rightarrow \text{Mo} = \text{O} + \text{NO}_2^{−}
\]

A brief illustration. The rate constant for the oxidation of the Ru(II) centre by the Co(III) centre in the bimetallic complex (18) is \(1.0 \times 10^9\) dm\(^3\) mol\(^{−}\) s\(^{−}\), whereas the rate constant for complex (19) is \(1.6 \times 10^9\) dm\(^3\) mol\(^{−}\) s\(^{−}\). In both complexes there is a pyridine carboxylic acid group bridging the two metal centres. These groups are bound to both metal atoms and could facilitate an

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\(^{4}\)Some bridged intermediates have been isolated with the electron clearly located on the bridge, but we shall not consider these here.
21.12 The outer-sphere mechanism

**Key points:** An outer-sphere redox reaction involves electron tunnelling between two reactants without any major disturbance of their covalent bonding or inner coordination spheres; the rate constant depends on the electronic and geometrical structures of the reacting species and on the Gibbs energy of reaction.

A conceptual starting point for understanding the principles of outer-sphere electron transfer is the deceptively simple reaction called electron self-exchange. A typical example is the exchange of an electron between \([\text{Fe(OH}_2\text{)}_6]^{3+}\) and \([\text{Fe(OH}_2\text{)}_6]^{2+}\) ions in water.

\[
[\text{Fe(OH}_2\text{)}_6]^{3+} + [\text{Fe(OH}_2\text{)}_6]^{2+} \rightarrow [\text{Fe(OH}_2\text{)}_6]^{2+} + [\text{Fe(OH}_2\text{)}_6]^{3+}
\]

Self-exchange reactions can be studied over a wide dynamic range with techniques ranging from isotopic labelling to NMR, with EPR being useful for even faster reactions. The rate constant of the Fe\(^{3+}/\text{Fe}^{2+}\) reaction is about 1 dm\(^3\) mol\(^{-1}\) s\(^{-1}\) at 25°C.

To set up a scheme for the mechanism, we invoke the Franck-Condon principle introduced originally to account for the vibrational structure of electronic transitions in spectroscopy, which states that electronic transitions are so fast that they take place in a stationary nuclear framework. In Fig. 21.18 the nuclear motions associated with the ‘reactant’ Fe\(^{3+}\) and its ‘conjugate product’ Fe\(^{2+}\) are represented as displacements along a reaction coordinate. If \([\text{Fe(OH}_2\text{)}_6]^{3+}\) lies at its energy minimum, then an instantaneous electron transfer would give a compressed state of \([\text{Fe(OH}_2\text{)}_6]^{2+}\). Likewise, the removal of an electron from Fe\(^{2+}\) at its energy minimum would give an expanded state of \([\text{Fe(OH}_2\text{)}_6]^{3+}\). The only instant at which the electron can transfer within the precursor complex is when both \([\text{Fe(OH}_2\text{)}_6]^{3+}\) and \([\text{Fe(OH}_2\text{)}_6]^{2+}\) have achieved the same nuclear configuration by thermally induced fluctuations. That configuration corresponds to the point of intersection of the two curves, and the energy required to reach this position is the Gibbs energy of activation, \(\Delta G\). If \([\text{Fe(OH}_2\text{)}_6]^{3+}\) and \([\text{Fe(OH}_2\text{)}_6]^{2+}\) differ in their nuclear configurations, \(\Delta G\) is larger and electron exchange is slower. The difference in rates is expressed quantitatively by the Marcus equation

\[
k_{ET} = v_N \kappa e^{-\Delta G/RT}
\]

where \(k_{ET}\) is the rate constant for electron transfer and \(\Delta G\) is given by

\[
\Delta G = \Delta G^\ddagger + \lambda \left[1 + \lambda \frac{\Delta G^\ddagger}{\lambda} \right]^{-2}
\]

with \(\Delta G^\ddagger\) the standard reaction Gibbs energy (which is obtained from the difference in standard potentials of the redox partners) and \(\lambda\) the reorganization energy, the energy required to move the nuclei associated with the reactant to the positions they adopt in the product immediately before the transfer of the electron. This energy depends on the changes in metal–ligand bond lengths (the so-called inner-sphere reorganization energy) and alterations in solvent polarization, principally the orientation of the solvent molecules around the complex (the outer-sphere reorganization energy).

The pre-exponential factor in eqn 21.14 has two components, the nuclear frequency factor \(v_N\) and the electronic factor \(\kappa\). The former is the frequency at which the two complexes, having already encountered each other in the solution, attain the transition state. The electronic factor gives the probability on a scale from 0 to 1 that an electron will transfer when the transition state is reached; its precise value depends on the extent of overlap of the donor and acceptor orbitals.

A small reorganization energy and a value of \(\kappa\) close to 1 corresponds to a redox couple capable of fast electron self-exchange. The first requirement is achieved if the transferred electron-transfer process through the bridge, suggesting an innershphere process. The fact that the rate constant changes between the two complexes, when the only substantive difference between them is in the substitution pattern of the pyridine ring, confirms that the bridge must be playing a role in the electron transfer process.

\[\text{Figure 21.17} \quad \text{Electron transfer between two metal ions in a precursor complex is not productive until their coordination shells have reorganized to be of equal size.} \]

\[\text{Figure 21.18} \quad \text{The potential energy curves for electron self-exchange. The nuclear motions of both the oxidized and reduced species (shown displaced along the reaction coordinate) and the surrounding solvent are represented by potential wells.} \]

\[\text{Figure 21.19} \quad \text{Nuclear coordinates} \]

\[\text{Tunnelling refers to a process where, according to classical physics, the electrons do not have sufficient energy to overcome the barrier but penetrate into or through it.} \]
electron is removed from or added to a nonbonding orbital, as the change in metal—ligand bond length is then least. It is also likely if the metal ion is shielded from the solvent, in the sense of it being sterically difficult for solvent molecules to approach close to the metal ion, because the polarization of the solvent is normally a major component of the reorganization energy. Simple metal ions such as aqua species typically have \( \lambda \) well in excess of 1 eV, whereas buried redox centres in enzymes, which are very well shielded from the solvent, can have values as low as 0.25 eV. A value of \( \kappa \) close to 1 is achieved if there is good orbital overlap between the two components of the precursor complex.

For a self-exchange reaction, \( \Delta G^e \) = 0 and therefore, from eqn 21.15, \( \Delta G = \frac{1}{4} \lambda \) and the rate of electron transfer is controlled by the reorganization energy (Fig. 21.19a). To a considerable extent, the rates of self-exchange can be interpreted in terms of the types of orbitals involved in the transfer (Table 21.12). In the \([\text{Cr}(\text{OH}_2)_6]^{3+/2+}\) self-exchange reaction, an electron is transferred between antibonding \( \sigma^* \) orbitals, and the consequent extensive change in metal—ligand bond lengths results in a large inner-sphere reorganization energy and therefore a slow reaction. The \([\text{Co}(\text{NH}_3)_6]^{3+/2+}\) couple has an even greater reorganization energy because two electrons are moved into the \( \sigma^* \) orbital as rearrangement occurs and the reaction is even slower. With the other hexaaqua and hexaammine complexes in the table, the electron is transferred between weakly antibonding or nonbonding \( \pi \) orbitals, the inner-sphere reorganization is less extensive, and the reactions are faster. The bulky, hydrophobic chelating ligand bipyridyl acts as a solvent shield, thus decreasing the outer-sphere reorganization energy.

Bipyridyl and other \( \pi \)-acceptor ligands allow electrons in an orbital with \( \pi \) symmetry on the metal ion to delocalize on to the ligand. This delocalization effectively lowers the reorganization energy when the electron is transferred between \( \pi \) orbitals, as occurs with Fe and Ru, where the electron transfer is between \( \pi \) orbitals (which, as explained in Section 20.2, can participate in \( \pi \) bonding), but not with Ni, where the electron transfer is between \( \text{e}^* \) orbitals. Delocalization can also increase the electronic factor.

Self-exchange reactions are helpful for pointing out the concepts that are involved in electron transfer, but chemically useful redox reactions occur between different species and involve net electron transfer. For the latter reactions, \( \Delta G^e \) is nonzero and contributes to the rate through eqns 21.14 and 21.15. Provided \( |\Delta G^e| < |\lambda| \) eqn 21.15 becomes

\[
\Delta^\ddagger G = \lambda \left( 1 + \frac{\Delta G}{\lambda} \right)^2 = \lambda \left( 1 + \frac{2 \Delta G}{\lambda} \right) \approx \lambda + 2 \Delta G
\]

and then according to eqn 21.14

\[
k_{\text{ET}} = \nu_n \kappa^e \exp\left[ -\left( \frac{\lambda + 2 \Delta G^e}{RT} \right) \right]
\]

Because \( \lambda > 0 \) and \( \Delta G^e < 0 \) for thermodynamically feasible reactions, provided \( |\Delta G^e| < |\lambda| \) the rate constant increases exponentially as \( \Delta G^e \) becomes increasingly favourable (that is, more negative). However, as \( |\Delta G^e| \) becomes comparable to \(|\lambda| \), this equation breaks down and we see that the reaction rate peaks before declining as \( |\Delta G^e| > |\lambda| \).

Equation 21.15 shows that \( \Delta^\ddagger G = 0 \) when \( \Delta G^e = -\lambda \). That is, the reaction becomes ‘activationless’ when the standard reaction Gibbs energy and the reorganization energy

![Figure 21.19](image)

**Figure 21.19** Variation of the activation Gibbs energy \( (\Delta^\ddagger G) \) with reaction Gibbs energy \( (\Delta G^e) \). (a) In a self-exchange reaction, \( \Delta G^e = 0 \) and \( \Delta G = \lambda/4 \). (b) A reaction is ‘activationless’ when \( \Delta G^e = -\lambda \). (c) \( \Delta G \) increases (the rate diminishes) as \( \Delta G^e \) becomes more negative beyond \( \Delta G^e = -\lambda \).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Electron configuration</th>
<th>( \Delta d/\text{pm} )</th>
<th>( k_{\text{ET}}/ (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cr}(\text{OH}_2)_6]^{3+/2+})</td>
<td>( t^1_{2g}/t^1_{2g} )</td>
<td>20</td>
<td>( 1 \times 10^{-5} )</td>
</tr>
<tr>
<td>([\text{VO}(\text{OH}_2)_6]^{3+/2+})</td>
<td>( t^2_{2g}/t^2_{2g} )</td>
<td>13</td>
<td>( 1 \times 10^{-5} )</td>
</tr>
<tr>
<td>([\text{Fe}(\text{OH}_2)_6]^{3+/2+})</td>
<td>( t^2_{2g}/t^2_{2g} )</td>
<td>13</td>
<td>( 1 )</td>
</tr>
<tr>
<td>([\text{Ru}(\text{OH}_2)_6]^{3+/2+})</td>
<td>( t^2_{2g}/t^2_{2g} )</td>
<td>9</td>
<td>( 20 )</td>
</tr>
<tr>
<td>([\text{Ru}(\text{NH}_3)_6]^{3+/2+})</td>
<td>( t^2_{2g}/t^2_{2g} )</td>
<td>4</td>
<td>( 9.6 \times 10^2 )</td>
</tr>
<tr>
<td>([\text{Co}(\text{NH}_3)_6]^{3+/2+})</td>
<td>( t^2_{2g}/t^2_{2g} )</td>
<td>22</td>
<td>( 2 \times 10^4 )</td>
</tr>
<tr>
<td>([\text{Fe}(\text{bpy})_3]^{3+/2+})</td>
<td>( t^2_{2g}/t^2_{2g} )</td>
<td>0</td>
<td>( 3 \times 10^4 )</td>
</tr>
<tr>
<td>([\text{Ru}(\text{bpy})_3]^{3+/2+})</td>
<td>( t^2_{2g}/t^2_{2g} )</td>
<td>0</td>
<td>( 4 \times 10^4 )</td>
</tr>
<tr>
<td>([\text{Ni}(\text{bpy})_3]^{3+/2+})</td>
<td>( t^2_{2g}/t^2_{2g} )</td>
<td>12</td>
<td>( 1.5 \times 10^5 )</td>
</tr>
</tbody>
</table>
cancel (Fig. 21.19b). The activation energy now increases as $\Delta G^\circ$ becomes more negative and the reaction rate decreases. This slowing of the reaction as the standard Gibbs energy of the reaction becomes more exergonic is called inverted behaviour (Fig. 21.19c). Inverted behaviour has important consequences, a notable one relating to the long-range electron transfer involved in photosynthesis. Photosystems are complex proteins containing light-excitible pigments such as chlorophyll and a chain of redox centres having low reorganization energies. In this chain, one highly exergonic recombination of the photoelectron with oxidized chlorophyll is sufficiently retarded (to 30 ns) to allow the electron to escape (in 200 ps) and proceed down the photosynthetic electron-transport chain, ultimately to produce reduced carbon compounds (Section 27.10). The theoretical dependence of the reaction rate of a reaction on the standard Gibbs energy is plotted in Fig. 21.20, and Fig. 21.21 shows the observed variation of reaction rate with $\Delta G^\circ$ for the iridium complex (20). The results plotted in Fig. 21.21 represent the first unambiguous experimental observation of an inverted region for a synthetic complex.

The Marcus equation can be used to predict the rate constants for outer-sphere electron transfer reactions between different species. Consider the electron-transfer reaction between an oxidant Ox and reductant Red:

$$\text{Ox}_1 + \text{Red}_2 \rightarrow \text{Red}_1 + \text{Ox}_2$$

If we suppose that the reorganization energy for this reaction is the average of the values for the two self-exchange processes, we can write $\lambda_{12} = \frac{1}{2}(\lambda_{11} + \lambda_{22})$ and then manipulation of eqns 21.14 and 21.15 gives the Marcus cross-relation

$$k_{12} = (k_{11}k_{22}K_{13}f_{12})^{1/2}$$

(21.16)

in which $k_{12}$ is the rate constant, $K_{13}$ is the equilibrium constant obtained from $\Delta G^\circ$ and $k_{11}$ and $k_{22}$ are the respective self-exchange rate constants for the two reaction partners. For reactions between simple ions in solution, when the standard Gibbs reaction energy is not too large, an LFER of the kind expressed by eqn 21.12 exists between $\Delta G$ and $\Delta G^\circ$ and $f_{12}$ can normally be set to 1. However, for reactions that are highly favourable thermodynamically (that is, $\Delta G^\circ$ large and negative) the LFER breaks down. The term $f_{12}$ takes into consideration the nonlinearity of the relationship between $\Delta G$ and $\Delta G^\circ$ and is given by

$$\log f_{12} = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/Z^2)}$$

(21.17)

where $Z$ is the constant of proportionality between the encounter density in solution (in moles of encounters per cubic decimetre per second) and the molar concentrations of the reactants; it is often taken to be $10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

### A brief illustration

The rate constants for

$$[\text{Co(bpy)}]^{3+} + [\text{Co(bpy)}]^{3+} \rightarrow [\text{Co(bpy)}]^{2+} + [\text{Co(bpy)}]^{2+}$$

$$[\text{Co(terpy)}]^{2+} + [\text{Co(terpy)}]^{3+} \rightarrow [\text{Co(terpy)}]^{3+} + [\text{Co(terpy)}]^{2+}$$

(where bpy is bipyridyl and terpy is tripyridyl) are $k_{11} = 9.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{22} = 48 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $K_{13} = 3.57$. Then for the outersphere reduction of $[\text{Co(bpy)}]^{3+}$ by $[\text{Co(terpy)}]^{2+}$, eqn 21.16 with $f_{12} = 1$ (as noted above) gives

$$k_{12} = (9.0 \times 48 \times 3.57)^{1/2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 39 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

This result compares reasonably well with the experimental value, which is $64 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. ■

---

**Figure 21.20** The theoretical dependence of the $\log k$ against $-\Delta G^\circ$ for a redox reaction with $\lambda = 1.0 \text{ eV} (96.5 \text{ kJ mol}^{-1})$.

**Figure 21.21** Plot of $\log k$ against $-\Delta G^\circ$ for the iridium complex (18) in acetonitrile solution at room temperature. The rates are for electron transfer from the photoexcited Ir$_2$ unit to the outlying pyridinium functionalities. (Data from L.S. Fox, M. Kozik, J.R. Winkler, and H.B. Gray, Science 1990, 247, 1069).
Photochemical reactions

The absorption of a photon of ultraviolet radiation or visible light increases the energy of a complex by between 170 and 600 kJ mol\(^{-1}\). Because these energies are larger than typical activation energies, it should not be surprising that new reaction channels are opened. However, when the high energy of a photon is used to provide the energy of the primary forward reaction, the back reaction is almost always very favourable, and much of the design of efficient photochemical systems lies in trying to avoid the back reaction.

21.13 Prompt and delayed reactions

**Key point:** Reactions of electronically excited species are classified as prompt or delayed.

In some cases, the excited state formed after absorption of a photon dissociates almost immediately after it is formed. Examples include formation of the pentacarbonyl intermediates that initiate ligand substitution in metal carbonyl compounds:

\[
\text{Cr(CO)}_6 \xrightarrow{hv} \text{Cr(CO)}_5 + \text{CO}
\]

and the scission of Co–Cl bonds:

\[
[\text{Co}^{3+}\text{Cl}(\text{NH}_3)_4]^{2+} \xrightarrow{hv} [\text{Co}^{2+}(\text{NH}_3)_4]^{3+} + \text{Cl}^{-}
\]

Both processes occur in less than 10 ps and hence are called prompt reactions.

In the second reaction, the quantum yield, the amount of reaction per mole of photons absorbed, increases as the wavelength of the radiation is decreased (and the photon energy correspondingly increased, \(E_{\text{photon}} = hc/\lambda\)). The energy in excess of the bond energy is available to the newly formed fragments and increases the probability that they will escape from each other through the solution before they have an opportunity to recombine.

Some excited states have long lifetimes. They may be regarded as energetic isomers of the ground state that can participate in delayed reactions. The excited state of \([\text{Ru}^{2+}(\text{bpy})_3]^{2+}\) created by photon absorption in the metal-to-ligand charge-transfer band (Section 20.5) may be regarded as a Ru(III) cation complexed to a radical anion of the ligand. Its redox reactions can be explained by adding the excitation energy (expressed as a potential by means of the molar excitation energy) to the ground-state reduction potential (Fig. 21.22).

21.14 \(d\)–\(d\) and charge-transfer reactions

**Key point:** A useful first approximation is to associate photosubstitution and photoisomerization with \(d\)–\(d\) transitions and photoredox reactions with charge-transfer transitions, but the rule is not absolute.

There are two main types of spectroscopically observable electron promotion in \(d\)-metal complexes, namely \(d\)–\(d\) transitions and charge-transfer transitions (Sections 20.4 and 20.5). A \(d\)–\(d\) transition corresponds to the essentially angular redistribution of electrons within a d shell. In octahedral complexes, this redistribution often corresponds to the occupation of M–L antibonding \(e_g^1\) orbitals. An example is the \(^3T_{2g} \leftrightarrow ^1A_{2g}\) transition in \([\text{Cr}(\text{NH}_3)_6]^{3+}\). The occupation of the antibonding \(e_g^1\) orbital results in a quantum yield close to 1 (specifically 0.6) for the photosubstitution

\[
[\text{Cr}(\text{NH}_3)_6]^{3+} + \text{H}_2\text{O} \xrightarrow{hv} [\text{Cr}(\text{NH}_3)_5(\text{OH})_2]^{3+} + \text{NH}_3
\]

This is a prompt reaction, as it occurs in less than 5 ps.

Charge-transfer transitions correspond to the radial redistribution of electron density. They correspond to the promotion of electrons into predominantly ligand orbitals if the transition is metal-to-ligand or into orbitals of predominantly metal character if the transition is ligand-to-metal. The former process corresponds to oxidation of the metal centre and the latter to its reduction. These excitations commonly initiate photoredox reactions of the kind already mentioned in connection with Co(III) and Ru(II).
Although a useful first approximation is to associate photosubstitution and photoisomerization with d→d transitions and photoredox with charge-transfer transitions, the rule is not absolute. For example, it is not uncommon for a charge-transfer transition to result in photosubstitution by an indirect path:

\[
\text{[Co}^{III}\text{Cl(NH}_3\text{)}_2\text{]}^{3+} + \text{H}_2\text{O} \rightarrow \text{[Co}^{II}\text{(NH}_3\text{)}_3\text{(OH}_2\text{)}\text{]}^{2+} + \text{Cl}^- \\
\text{[Co}^{II}\text{(NH}_3\text{)}_3\text{(OH}_2\text{)}\text{]}^{2+} + \text{Cl}^- \rightarrow \text{[Co}^{III}\text{(NH}_3\text{)}_3\text{(OH}_2\text{)}\text{]}^{3+} + \text{Cl}^- \]

In this case, the aqua complex formed after the homolytic fission of the Co–Cl bond is reoxidized by the Cl atom. The net result leaves the Co substituted. Conversely, some excited states show no differences in substitutational reactivity compared with the ground state: the long-lived excited \(^2\text{E}\) state of \([\text{Cr(bpy)}_3]^{3+}\) results from a pure d→d transition and its lifetime of several microseconds allows the excess energy to enhance its redox reactions. The standard potential (+1.3 V), calculated by adding the excitation energy to the ground-state value, accounts for its function as a good oxidizing agent, in which it undergoes reduction to \([\text{Cr(bpy)}_3]^{2+}\).

### 21.15 Transitions in metal–metal bonded systems

**Key points:** Population of a metal–metal antibonding orbital can sometimes initiate photodissociation; such excited states have been shown to initiate multielectron redox photochemistry.

We might expect the \(\delta^* \leftarrow \delta\) transition in metal–metal bonded systems to initiate photodissociation as it results in the population of an antibonding orbital of the metal–metal system. It is more interesting that such excited states have also been shown to initiate multi-electron redox photochemistry.

One of the best characterized systems is the dinuclear platinum complex \([\text{Pt}_4\text{(μ-P}_2\text{O}_2\text{H}_2\text{)}_4]^{4+}\), called informally ‘PtPOP’ (21). There is no metal–metal bonding in the ground state of this \(\text{Pt(II)}–\text{Pt(II)}\) \(d^8–d^8\) species. The HOMO–LUMO pattern indicates that excitation populates a bonding orbital between the two metal atoms (Fig. 21.23). The lowest-lying excited state has a lifetime of 9 \(\mu\)s and is a powerful reducing agent, reacting by both electron and halogen-atom transfer. The most interesting oxidation products are \(\text{Pt(III)}–\text{Pt(III)}\), which contain \(X^-\) ligands (where \(X\) is halogen or pseudohalogen) at both ends and a metal–metal single bond. Irradiation in the presence of \((\text{Bu})_3\text{SnH}\) gives a dihydrido product that can eliminate \(\text{H}_2\).

Irradiation of the quadruply bonded dinuclear cluster \([\text{Mo}_4\text{(O}_2\text{P(OC}_6\text{H}_5\text{)}_2\text{)}_4]^{22}\) at 500 nm in the presence of \(\text{ClICH}_2\text{CH}_2\text{Cl}\) results in production of ethene and the addition of two \(\text{Cl}\) atoms to the two \(\text{Mo}\) atoms, with a two-electron oxidation. The reaction proceeds in one-electron steps, and requires a complex with the metal atoms shielded by sterically crowding ligands. If smaller ligands are present, the reaction that occurs instead is a photochemical oxidative addition of the organic molecule.

**Figure 21.23** The dinuclear complex \([\text{Pt}_4\text{(μ-P}_2\text{O}_2\text{H}_2\text{)}_4]^{4+}\) consists of two face-to-face square-planar complexes held together by a bridging pyrophosphito ligand. The metal \(p\) and \(d\) orbitals interact along the Pt–Pt axis. The other \(p\) and \(d\) orbitals are considered to be nonbonding. Photoexcitation results in an electron in the antibonding \(\sigma^*\) orbital moving into the bonding \(\sigma\) orbital.
FURTHER READING


EXERCISES

21.1 The rate constants for the formation of [Co(NH₃)₆Cl]²⁺ from [Co(NH₃)₆(N₂)]³⁺ for X = Cl⁻, Br⁻, I⁻, and SCN⁻ differ by no more than a factor of two. What is the mechanism of the substitution?

21.2 If a substitution process is associative, why may it be difficult to characterize an aqua ion as labile or inert?

21.3 The reactions of Ni(CO)₅ in which phosphines or phosphites replace CO to give Ni(CO)₅ all occur at the same rate regardless of which phosphine or phosphite is being used. Is the reaction d or a?

21.4 Write the rate law for formation of [MnX(OH₂)₃]⁺ from the aqua ion and X⁻. How would you undertake to determine if the reaction is d or a?

21.5 Octahedral complexes of metal centres with high oxidation numbers or of d metals of the second and third series are less labile than those of low oxidation number and d metals of the first series of the block. Account for this observation on the basis of a dissociative rate-determining step.

21.6 A Pt(II) complex of tetramethyldiethylenetriamine is attacked by Cl⁻ 10⁻¹⁵ times less rapidly than the diethylenetriamine analogue. Explain this observation in terms of an associative rate-determining step.

21.7 The rate of loss of chlorobenzene, PhCl, from [W(CO)₅L][PhCl] increases with increase in the cone angle of L. What does this observation suggest about the mechanism?

21.8 The pressure dependence of the replacement of chlorobenzene (PhCl) by piperidine in the complex [W(CO)₅(PhH)(PhCl)] has been studied. The volume of activation is found to be +11.3 cm³ mol⁻¹. What does this value suggest about the mechanism?

21.9 Does the fact that [Ni(CN)₅]¹⁺ can be isolated help to explain why substitution reactions of [Ni(CN)₅]²⁻ are very rapid?

21.10 Reactions of [Pt(Ph)₅(SMe)₂] with the bidentate ligand 1,10-phenanthroline (phen) give [Pt(Ph)phen]. There is a kinetic pathway with activation parameters ΔH = +101 kJ mol⁻¹ and ΔS = +42 J K⁻¹ mol⁻¹. Propose a mechanism.

21.11 Design two-step syntheses of cis- and trans-[PtCl₂(NO₂)(NH₃)]⁺ starting from [PtCl₄]²⁻.

21.12 How does each of the following modifications affect the rate of a square-planar complex substitution reaction? (a) Changing a trans ligand from H to Cl. (b) Changing the leaving group from Cl to I. (c) Adding a bulky substituent to a cis ligand. (d) Increasing the positive charge on the complex.

21.13 The rate of attack on Co(III) by an entering group Y is nearly independent of Y with the spectacular exception of the rapid reaction with OH⁻. Explain the anomaly. What is the implication of your explanation for the behaviour of a complex lacking Brønsted acidity on the ligands?

21.14 Predict the products of the following reactions:

(a) [Pt(PR₃)₃]²⁻ + 2 Cl⁻
(b) [PtCl₄]²⁻ + 2 PR₃
(c) cis-[Pt(NH₃)₄(py)]²⁺ + 2 Cl⁻

21.15 Put in order of increasing rate of substitution by H₂O the complexes (a) [Co(NH₃)₆]³⁺, (b) [Rh(NH₃)₆]³⁺, (c) [Ir(NH₃)₆]³⁺, (d) [Mn(OH₂)₆]²⁺, (e) [Ni(OH₂)₆]³⁺.

21.16 State the effect on the rate of dissociatively activated reactions of Rh(III) complexes of (a) an increase in the overall charge on the complex, (b) changing the leaving group from NO₂ to Cl⁻, (c) changing the entering group from Cl⁻ to I⁻, (d) changing the cis ligands from NH₃ to H₂O.

21.17 Write out the inner- and outer-sphere pathways for reduction of azidopentamminecobalt(III) ion with V³⁻(aq). What experimental data might be used to distinguish between the two pathways?

21.18 The compound [Fe(SCN)(OH₂)₆]³⁻ can be detected in the reaction of [Co(NCS)(NH₃)₅]²⁺ with Fe²⁺(aq) to give Fe³⁺(aq) and Co³⁺(aq). What does this observation suggest about the mechanism?

21.19 Calculate the rate constants for electron transfer in the oxidation of [V(OH₂)₄]³⁻ (E°(V³⁻/V²⁻) = −0.255 V) and the oxidants (a) [Ru(NH₃)₆]³⁺ (E°(Ru³⁺/Ru²⁺) = +0.07 V), (b) [Co(NH₃)₆]³⁺ (E°(Co³⁺/Co²⁺) = +0.10 V). Comment on the relative sizes of the rate constants.

21.20 Calculate the rate constants for electron transfer in the oxidation of [Cr(OH₂)₆]³⁺ (E°(Cr³⁺/Cr²⁺) = −0.41 V) and each of the oxidants [Ru(NH₃)₆]³⁺ (E°(Ru³⁺/Ru²⁺) = +0.07 V), [Fe(OH₂)₄]³⁻ (E°(Fe³⁺/Fe²⁺) = +0.77 V) and [Ru(bpy)₃]³⁺ (E°(Ru³⁺/Ru²⁺) = +1.26 V). Comment on the relative sizes of the rate constants.

21.21 The photochemical substitution of [W(CO)₅(py)]⁺ (py = pyridine) with triphenylphosphine gives W(CO)₅(P(C₃H₅)₃). In the presence of excess phosphine, the quantum yield is approximately 0.4. A flash photolysis study reveals a spectrum that can be assigned to the intermediate W(CO)₅(P(C₃H₅)₃). What product and quantum yield do you predict for substitution of [W(CO)₅(py)]⁺ in the presence of excess triethylamine? Is this reaction expected to be initiated from the ligand field or MLCT excited state of the complex?

21.22 From the spectrum of [CrCl(NH₃)₅]Cl⁺ shown in Fig. 20.32, propose a wavelength for photoionization of reduction of Cr(III) to Cr(II) accompanied by oxidation of a ligand.
**PROBLEMS**

21.1 Given the following mechanism for the formation of a chelate complex:

\[
\begin{align*}
\text{[Ni(OH)}_2\text{]}^{2+} + L - L &\rightleftharpoons \text{[Ni(OH)}_2\text{]}^{2+}L - L \quad K_{\text{eq}} \text{ rapid} \\
\text{[Ni(OH)}_2\text{]}^{2+}L - L &\rightleftharpoons \text{[Ni(OH)}_2\text{]}^{2+}L - L + H_2O \quad k_1, k_1' \\
\text{[Ni(OH)}_2\text{]}^{2+}L - L &\rightleftharpoons \text{[Ni(OH)}_2\text{]}^{2+}L - L + H_2O \quad k_2, k_2'
\end{align*}
\]

derive the rate law for the formation of the chelate. Discuss the step that is different from that for two monodentate ligands. The formation of chelates with strongly bound ligands occurs at the rate of formation of the analogous monodentate complex but the formation of chelates of weakly bound ligands is often significantly slower. Assuming an $I_2$ mechanism, explain this observation. (See R.G. Wilkins, *Acc. Chem. Res.*, 1970, 3, 408.)

21.2 The complex [PtH(P Et$_3$)$_2$]$^+$ was studied in deuterated acetone in the presence of excess P Et$_3$. In the absence of excess ligand the 1H-NMR spectrum in the hydride region exhibits a doublet of triplets. As excess P Et$_3$ ligand is added the hydride signal begins to change, the line shape depending on the ligand concentration. Suggest a mechanism to account for the effects of excess P Et$_3$.

21.3 Solutions of [PtH$_2$(P Me$_3$)$_2$] exist as a mixture of cis and trans isomers. Addition of excess P Me$_3$ led to formation of [PtH$_2$(P Me$_3$)$_2$] at a concentration that could be detected using NMR. This complex exchanged phosphine ligands rapidly with the trans isomer but not the cis. Propose a pathway. What are the implications for the trans effect of H versus P Me$_3$? (See D.L. Packett and W.G. Trogler, *Inorg. Chem.*, 1988, 27, 1768.)

21.4 Figure 21.24 (which is based on J.B. Goddard and F. Basolo, *Inorg. Chem.*, 1968, 7, 936) shows the observed first-order rate constants for the reaction of [PdBrL]$_2$ with various Y to give [PdYL]$_2$, where L is Et$_3$ NCH$_2$CH$_2$NHCH$_2$CH$_2$NEt$_2$. Note the large slope for $S_O^-$ and zero slopes for $Y = N_3^-$, $I^-$, NO$_2^-$, and SCN$^-$. Propose a mechanism.

![Figure 21.24](image)

**Figure 21.24** The data required for Problem 21.4.

21.5 The substitution reactions of the bridged dinuclear Rh(II) complex [Rh$_2$(μ-O$_2$)CH$_2$CH$_2$]$_2$(XY) (23) have been studied by M.A.S. Aquino and D.H. Macartney (*Inorg. Chem.*, 1987, 26, 2696). Reaction rates show little dependence on the choice of the entering group. The table below shows the dependence on the leaving group, X, and the ligand on the opposite Rh, (trans) Y, at 298K. What conclusions can you draw concerning the mechanism? Note that the complex has a d$^9$ configuration at each Rh and a single Rh–Rh bond.

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>$k_2/(dm^3\cdot mol^{-1}\cdot s^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>CH$_3$OH</td>
<td>$2 \times 10^6$</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>CH$_3$CN</td>
<td>$1.1 \times 10^6$</td>
</tr>
<tr>
<td>PPh$_3$</td>
<td>PPh$_3$</td>
<td>$1.5 \times 10^5$</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>PR$_3$</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>PR$_3$</td>
<td>CH$_3$CN</td>
<td>$10^{-1} - 10^0$</td>
</tr>
<tr>
<td>N-donor</td>
<td>H$_2$O</td>
<td>$10^0 - 10^1$</td>
</tr>
</tbody>
</table>

21.6 The activation enthalpy for the reduction of cis-[CoCl$_2$(en)$_2$]$^+$ by Cr$^{3+}$(aq) is $-24$ kJ mol$^{-1}$. Explain the negative value. (See R.C. Patel, R.E. Ball, J.F. Endicott, and R.G. Hughes, *Inorg. Chem.*, 1970, 9, 23.)

21.7 The rate of reduction of [Co(NH$_3$)$_3$(OH)$_2$]$^{3+}$ by Cr(II) is seven orders of magnitude slower than reduction of its conjugate base, [Co(NH$_3$)$_3$(OH)$_2$]$^{2+}$, by Cr(II). For the corresponding reductions with [Ru(NH$_3$)$_3$]$^{3+}$, the two differ by less than a factor of 10. What do these observations suggest about mechanisms?

21.8 Consider the complexes (18) and (19) discussed in the illustration on page 526. Think about the potential routes of the electron transfer in the two complexes and suggest why there is such a difference in the rates of electron transfer between the two complexes.

21.9 Calculate the rate constants for outer-sphere reactions from the following data. Compare your results to the measured values in the last column.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_2/(dm^3\cdot mol^{-1}\cdot s^{-1})$</th>
<th>$E^{\circ} \cdot V$</th>
<th>$k_3/(dm^3\cdot mol^{-1}\cdot s^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$^{3+}$ + Fe$^{2+}$</td>
<td>$2 \times 10^{-5}$</td>
<td>+1.18</td>
<td>2.3 $\times 10^1$</td>
</tr>
<tr>
<td>[W(CN)$_6$]$^{3-}$ + Ce(IV)</td>
<td>$&gt;4 \times 10^4$</td>
<td>4.4</td>
<td>+0.90</td>
</tr>
<tr>
<td>[Fe(CN)$_6$]$^{3-}$ + MnO$_4^-$</td>
<td>$7.4 \times 10^4$</td>
<td>$3 \times 10^1$</td>
<td>+0.20</td>
</tr>
<tr>
<td>[F(phen)$_2$]$^{3-}$ + Ce(IV)</td>
<td>$&gt;3 \times 10^5$</td>
<td>4.4</td>
<td>+0.36</td>
</tr>
</tbody>
</table>

21.10 In the presence of catalytic amounts of [Pt(P$_2$O$_5$)$_2$(H)$_2$]$^{4+}$ (21) and light, 2-propanol produces H$_2$ and acetone (E.L. Harley, A.E. Stiegler, A. Vlcek, Jr., and H.B. Gray, *J. Am. Chem. Soc.*, 1987, 109, 5233; D.C. Smith and H.B. Gray, *Coord. Chem. Rev.*, 1990, 100, 169). (a) Give the equation for the overall reaction. (b) Give a plausible molecular orbital scheme for the metal–metal bonding in this tetrahedral-prismatic complex and indicate the nature of the excited state that is thought to be responsible for the photochemistry. (c) Indicate the metal complex intermediates and the evidence for their existence.