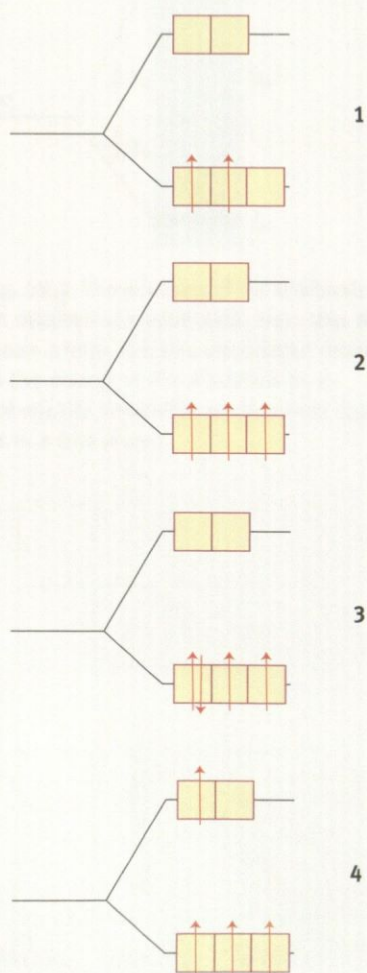


Table 19.2 Ligand-field stabilization energies*

d^n	Example	Octahedral		Tetrahedral	
		N	LFSE	N	LFSE
d^0		0	0	0	0
d^1	Ti ³⁺	1	0.4	1	0.6
d^2	V ³⁺	2	0.8	2	1.2
d^3	Cr ³⁺ , V ²⁺	3	1.2	3	0.8
		Strong-field		Weak-field	
d^4	Cr ²⁺ , Mn ³⁺	2	1.6	4	0.6
d^5	Mn ²⁺ , Fe ³⁺	1	2.0	5	0
d^6	Fe ²⁺ , Co ³⁺	0	2.4	4	0.4
d^7	Co ²⁺	1	1.8	3	0.8
d^8	Ni ²⁺	2	1.2	2	0.8
d^9	Cu ²⁺	1	0.6	1	0.4
d^{10}	Cu ⁺ , Zn ²⁺	0	0	0	0

* N is the number of unpaired electrons; LFSE is in units of Δ_O for octahedra or Δ_T for tetrahedra; the calculated relation is $\Delta_T \approx 0.45\Delta_O$.



configuration relative to the barycentre, which is called the **ligand-field stabilization energy (LFSE)**,³ is

$$\text{LFSE} = (0.4x - 0.6y)\Delta_O \quad (19.1)$$

Table 19.2 lists the LFSE values for various configurations. The LFSE is generally only a small fraction of the overall interaction between the metal atom and the ligands, which increases from left to right across a period on account of the decrease in radius of the M^{2+} ions along that series.

(c) Weak-field and strong-field limits

Key points: The ground-state configuration of a complex reflects the relative values of the ligand-field splitting parameter and the pairing energy; for $3d^n$ 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.

To obtain the ground-state electron configurations of d -metal complexes, we use the d -orbital energy level diagram shown in Fig. 19.2 as a basis for applying the building-up principle. We look for 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. We begin by considering 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} nonbonding orbitals, and do so with parallel spins. For example, the ions Ti²⁺ and V²⁺ have electron configurations $3d^2$ and $3d^3$, respectively. The d electrons occupy the lower t_{2g} orbitals as shown in (1) and (2), respectively, and the complexes are stabilized by $2 \times (0.4\Delta_O) = 0.8\Delta_O$ (for Ti²⁺) and $3 \times (0.4\Delta_O) = 1.2\Delta_O$ (for V²⁺).

The next electron needed for the $3d^4$ ion Cr²⁺ 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 Δ_O . In the first case (t_{2g}^4), the LFSE is $1.6\Delta_O$, the pairing energy is P , and the net stabilization is $1.6\Delta_O - P$. In the second case ($t_{2g}^3 e_g^1$), the LFSE is

³ 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.

$3 \times (0.4\Delta_O) - 0.6\Delta_O = 0.6\Delta_O$, and there is no pairing energy to consider. Which configuration is adopted depends on which of $1.60\Delta_O - P$ and $0.60\Delta_O$ is the larger.

If $\Delta_O < P$, which is called the **weak-field case**, a lower energy is achieved if the upper orbital is occupied to give the configuration $t_{2g}^3 e_g^1$. If $\Delta_O > P$, 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, $[\text{Cr}(\text{OH}_2)_6]^{2+}$ has the ground-state configuration $t_{2g}^3 e_g^1$ whereas $[\text{Cr}(\text{CN})_6]^{4-}$, with relatively strong-field ligands (as given by the spectrochemical series), has the configuration t_{2g}^4 .

The ground-state electron configurations of $3d^1$, $3d^2$, and $3d^3$ complexes are unambiguous because there is no competition between the LFSE and the pairing energy: the configurations are t_{2g}^1 , t_{2g}^2 , and t_{2g}^3 , respectively. There are two possible configurations for $3d^n$ complexes in which $n = 4$ or 5 : in the strong-field case the lower orbitals will be occupied, giving rise to t_{2g}^n configurations, whereas in the weak-field case electrons will avoid the pairing energy by occupying the upper orbitals, when the configurations will be $t_{2g}^3 e_g^1$ and $t_{2g}^3 e_g^2$. Because in the latter case all the electrons occupy different orbitals, they will have parallel spins.

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**. 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. 19.4). The same applies to $3d^5$ complexes (see Table 19.2). High- and low-spin configurations are also found for $3d^6$ and $3d^7$ complexes. In these cases, a strong crystal field results in the low-spin configurations t_{2g}^6 (no unpaired electrons) and $t_{2g}^5 e_g^1$ (one unpaired electron), respectively, and a weak crystal field results in the high-spin configurations $t_{2g}^4 e_g^2$ (four unpaired electrons) and $t_{2g}^5 e_g^2$ (three unpaired electrons), respectively.

The strength of the crystal field (as measured by the value of Δ_O) 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 d^n complexes with $n = 1-3$ and $8-10$ there is no ambiguity about the configuration (see Table 19.2), and the designations high-spin and low-spin are not used.

As we have seen, the values of Δ_O for complexes of $4d$ - and $5d$ -series metals are typically higher than for the $3d$ -series metals. 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 $4d^4$ complex $[\text{RuCl}_6]^{2-}$, which has a t_{2g}^4 configuration, corresponding to a strong crystal field, despite Cl^- being low in the spectrochemical series. Likewise, $[\text{Ru}(\text{ox})_3]^{3-}$ has the low-spin configuration t_{2g}^5 whereas $[\text{Fe}(\text{ox})_3]^{3-}$ has the high-spin configuration $t_{2g}^3 e_g^2$.

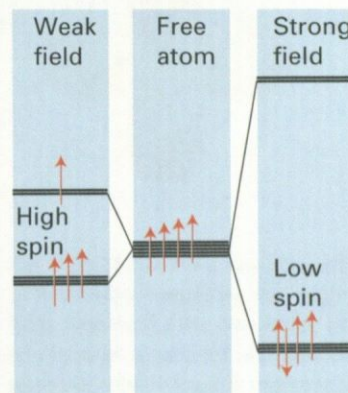


Fig. 19.4 The effect of weak and strong ligand fields on the occupation of electrons for a d^4 complex. The former results in a high-spin configuration and the latter in a low-spin configuration.

Example 19.1 Calculating the LFSE

What is the LFSE for octahedral ions of the following configurations: (a) d^3 , (b) high-spin d^5 (c) d^9 ?

Answer Using the notation $t_{2g}^x e_g^y$ and eqn 19.1, we can assign the following values: (a) $x = 3$, $y = 0$, therefore $\text{LFSE} = 1.2\Delta_O$, (b) $x = 3$, $y = 2$, therefore $\text{LFSE} = 0$, (c) $x = 6$, $y = 3$, therefore $\text{LFSE} = 0.6\Delta_O$.

Self test 19.1 What is the LFSE for both high- and low-spin d^6 configurations?

(d) Magnetic measurements

Key points: Magnetic measurements can be 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^5 and for high-spin $3d^6$ and $3d^7$ complexes.

Preface

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Inorganic Chemistry

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