17 Transition metals

17.1 (a) Using Slater's rules (page 262), determine the effective nuclear charge experienced by the 4*s* and 3*d* electrons in the metals of the first transition series (use the electronic configurations given in Fig. 17.1 on page 626). Compute the energies of the 4*s* and 3*d* orbitals using

$$E_n = -\frac{Z_{\text{eff}}^2 R_{\text{H}}}{n^2},$$

where $R_{\text{H}} = 13.6$ eV and n is the principal quantum number. On the same graph, plot these energies against atomic number.

(b) Comment on the trends that you see in your graph, and compare it with the data given in Fig. 17.2 on page 627.

(c) Repeat the calculations for the ion M^+, assuming that a 4*s* electron has been ionized. Comment on how the orbital energies for M^+ compare with those for M. According to your calculations, which electron will be the easiest to ionize to give M^{2+}?

17.2 Explain or rationalize the following.

(a) The ground-state electronic configuration of potassium is [Ar] $4s^1$ and not [Ar] $3d^1$.

(b) In titanium (Ti) the 3*d* AO is lower in energy than the 4*s*, yet the ground-state electronic configuration of Ti is $4s^2\,3d^2$ and not $3d^4$.

(c) The ground-state configuration of copper (Cu) is $4s^1\,3d^{10}$ rather than $4s^2\,3d^9$.

(d) Across the first transition series, the energy of the 4*s* orbital falls more slowly than does the energy of the 3*d*.

17.3 Throughout this question assume that the exchange interaction contributes an energy of $-K$ per pair of parallel spins (see section 2.7.3 on page 73).

(a) Show that the exchange contribution to the energy of the configuration $4s^2\,3d^3$ is $-6K$, and that the contribution for the configuration $4s^1\,3d^4$ is $-10K$.

(b) Work out the exchange contribution to the configurations $4s^2\,3d^4$, $4s^1\,3d^5$, $4s^2\,3d^5$ and $4s^1\,3d^6$

(c) By considering the *change* in the exchange contribution on going from $4s^2\,3d^n$ to $4s^1\,3d^{n+1}$, rationalize the ground-state configurations adopted by V, Cr and Mn.

17.4 (a) What do you understand by the *chelate effect*?

(b) For the following reaction

$$[\text{Ni(NH}_3)_6]^{2+} + 3\,\text{en} \longrightarrow [\text{Ni(en)}_3]^{2+} + 6\,\text{NH}_3$$

it is found that $\Delta_r H^\circ = -12.1$ kJ mol^{-1} and $\Delta_r S^\circ = 185$ J K^{-1} mol^{-1} in aqueous solution at 298 K. Compute the value of $\Delta_r G^\circ$ and hence the value of the equilibrium constant. Does the entropy term make a significant contribution to the value of $\Delta_r G^\circ$?

(c) Discuss the trend in the values of the equilibrium constant for the following reactions (all in aqueous solution)

$$\begin{array}{ll}
[\text{Co(H}_2\text{O)}_6]^{2+} + 6\,\text{NH}_3 \longrightarrow [\text{Co(NH}_3)_6]^{2+} + 6\,\text{H}_2\text{O} & \lg K = 5.2 \\
[\text{Co(H}_2\text{O)}_6]^{2+} + 3\,\text{en} \longrightarrow [\text{Co(en)}_3]^{2+} + 6\,\text{H}_2\text{O} & \lg K = 13.9 \\
[\text{Co(H}_2\text{O)}_6]^{2+} + (6\text{-en}) \longrightarrow [\text{Co(6-en)}]^{2+} + 6\,\text{H}_2\text{O} & \lg K = 15.8
\end{array}$$

(6-en) is a hexadentate ligand which coordinates through nitrogen.

17.5 (a) Draw two isomers of the octahedral complex $[Co(NH_3)_4Cl_2]^+$. Are either of these isomers optically active?

(b) Draw all the possible isomers of the octahedral complex $[Co(en)_2(NH_3)Cl]^{2+}$. Which of these are optically active?

(c) Draw all the possible isomers of the hypothetical octahedral complex $MA_2B_2C_2$, where A, B and C are three different monodentate ligands. Which, if any, of these isomers are optically active?

17.6 When carbon monoxide acts as a ligand to a transition metal it invariably bonds through the carbon and not through the oxygen. Discuss why this is so.

17.7 Using the same approach as in section 17.4 on page 639, show that for the d^6 configuration the high-spin arrangement is preferred when

$$2\Delta_o - 10K < -6K.$$

Similarly, show that for the d^7 configuration the high-spin arrangement is preferred when $\Delta_o < 2K$.

17.8 For paramagnetic first-row transition metal complexes the *magnetic moment* μ, in units of the *Bohr magneton* (B.M.), is reasonably well approximated by the spin-only formula

$$\text{magnetic moment in B.M.} = \sqrt{n(n+2)}$$

where n is the number of unpaired electrons. Use this expression to draw up a table of the expected magnetic moments for between one and five unpaired electrons. Then draw up a second table showing the expected magnetic moments for high-spin and for low-spin octahedral complexes with between one and nine d electrons.

Use the following experimentally measured magnetic moments to determine whether the given octahedral complex is high or low spin. [Be aware that the spin-only formula is not expected to give precise agreement with experimental data.]

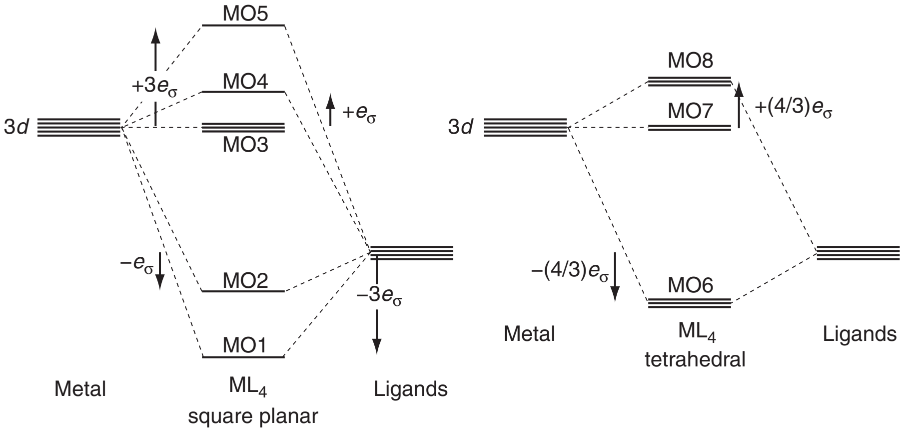
complex	μ / B.M.	complex	μ / B.M.
$[Co(NO_2)_6]^{4-}$	1.9	$[Cr(H_2O)_6]^{3+}$	3.8
$[Cr(H_2O)_6]^{2+}$	4.8	$[Mn(H_2O)_6]^{2+}$	5.9
$[Fe(CN)_6]^{3-}$	2.3	$[Fe(H_2O)_6]^{2+}$	5.3

In the complex $[Co(NO_2)_6]^{4-}$ the ligands are $[NO_2]^-$.

17.9 Using the approach described in section 17.6.1 on page 644, compute the change in energy due to the occupation of the $1e_g$, $1t_{2g}$ and $2e_g$ MOs as a function of the number of d electrons assuming that a *low-spin* configuration is adopted.

Plot a graph of this energy in the same form as Fig. 17.22 on page 645, and use it to predict how you would expect the energy of a low-spin complex to vary with the number of d electrons.

17.10 This question is about how the energy difference between a square planar and tetrahedral ML_4 complex varies with the number of d electrons. Shown below are partial MO diagrams for the two geometries: *only* those MOs which have a contribution from the metal orbitals are shown. Note that MO3, MO6 and MO8 are triply degenerate; MO7 is doubly degenerate.



A simplified MO treatment shows that the amount by which each MO is shifted in energy on forming the complex can be expressed in terms of a single energy parameter e_σ. For example, MO1 is shifted down in energy by $3e_\sigma$, whereas MO8 is shifted up in energy by $\frac{4}{3}\,e_\sigma$. MO3 and MO7 are nonbonding and so do not change energy.

In the square-planar geometry MO1 and MO2 are occupied by two electrons each, contributing an total energy change of $2\times(-3e_\sigma)+2\times(-e_\sigma) = -8e_\sigma$. Similarly in the tetrahedral geometry the triply degenerate MO6 is occupied by six electrons, contributing an total energy change of $6\times(-\frac{4}{3}e_\sigma) = -8e_\sigma$ i.e. exactly the same amount. In comparing the two geometries, we can therefore ignore these filled orbitals.

The electrons originating from the metal 3d AOs can fill MO3, MO4 and MO5 in the square-planar case, and MO7 and MO8 in the tetrahedral case. The precise details of which orbitals are occupied will determine the relative energy of the two possible geometries for ML_4.

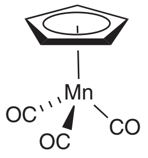
Consider the case of four d electrons. Assuming a high-spin configuration, in the square-planar complex three electrons will occupy the three degenerate orbitals MO3, which contribute nothing to the energy change, and one will occupy MO4, which contributes $+e_\sigma$. The energy change is thus $+e_\sigma$. In the tetrahedral case, two electrons occupy MO7 and two occupy MO8, so the energy change is $2\times 0 + 2\times(+\frac{4}{3}e_\sigma) = 2.67\,e_\sigma$. It is clear that the square-planar geometry is preferred since the energy increase due to the d electrons is smaller than that for the tetrahedral case.

(a) Repeat this calculation for between one and ten d electrons (assuming a high-spin configuration), and hence identify those configurations for which the square-planar geometry is preferred.

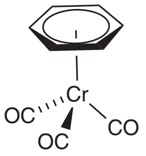
(b) Now consider the case where the square-planar complex is low spin (meaning that MO5 is not occupied until *both* MO3 *and* MO4 are full) but the tetrahedral complex is still high spin. Again identify those configurations for which the square-planar geometry is preferred.

(c) In the light of your calculations, comment on the fact that square-planar complexes are most commonly found for metals with d^8 configurations in conjunction with ligands which give rise to large splitting of the d orbitals.

17.11 Count the number of valence electrons associated with each metal atom in the following complexes (perform the count using the scheme in Box 17.1 on page 651 and then using the scheme in Box 17.2 on page 652).



$Mn(CO)_3(C_5H_5)$



$Cr(CO)_3(C_6H_6)$

17.12 Determine the number of carbon monoxide ligands which need to be attached to each transition metal atom from the first row in order that the eighteen-electron rule is obeyed by a complex $M(CO)_n$ or $[M(CO)_n]^+$.

17.13 (a) Comment on the fact that no mono-nuclear neutral cobalt carbonyl $Co(CO)_n$ has been detected, but the anion $[Co(CO)_4]^-$ is known.

(b) Reaction of cobalt with carbon monoxide gives the species $Co_2(CO)_8$ which is thought to exist in two structural isomers. The IR spectrum of isomer A shows a number of bands between 2000 cm^{-1} and 2100 cm^{-1}; the spectrum of isomer B shows bands in this same region as well as bands at around 1850 cm^{-1}.

Explain what you can deduce from the IR spectrum about the bonding of the CO groups in these two carbonyl complexes, and hence suggest possible structures for A and B. You should ensure that your structures are consistent with the eighteen-electron rule.

(c) The carbonyl complex $Co_4(CO)_{12}$ is also formed quite readily. Suggest a structure for this in which the eighteen-electron rule is obeyed [hint: start with a tetrahedron of cobalt atoms].

17.14 Discuss the following observations. MnO is a basic oxide, dissolving in aqueous acid to give the species $[Mn(H_2O)_6]^{2+}$. Similarly, Mn_2O_3 is also basic, dissolving in acid to give the aquated ion $[Mn(H_2O)_6]^{3+}$ which tends to be unstable with respect to disproportionation. MnO_2 is an amphoteric oxide; it dissolves in alkali to give the anion $[MnO_3]^{2-}$, but even in strongly acidic solutions there is no evidence for a simple aquo ion '$[Mn(H_2O)_6]^{4+}$'. Mn_2O_7 readily dissolves in and reacts with water to give strongly acidic solutions containing $[MnO_4]^-$.

17.15 Discuss the following observations. Even in the most acidic solutions there is no evidence for the Ti(IV) species '$[Ti(H_2O)_6]^{4+}$'. However, the species $[Ti(H_2O)_5(OH)]^{3+}$, $[Ti(H_2O)_4(OH)_2]^{2+}$ and $[Ti(H_2O)_3(OH)_3]^+$ have all been characterized. Some workers have also suggested the existence of the species $[TiO]^{2+}$ (with associated waters of solvation), but the evidence is not compelling (discuss how this species might be formed). In contrast, there is ample evidence for the existence of the vanadium(IV) species $[VO]^{2+}$. In this ion, the V–O bond length is around 160 pm, indicative of multiple bonding between these atoms.