
d-Block chemistry

Answers to worked examples

WE 28.1 Electronic configurations

Work out the electronic configuration of Co^{2+} and Co^+ .

Strategy

Write down the ground state configuration for a cobalt atom. Then place all of the 4s electrons into the 3d orbitals if they are available as the 3d orbitals are lower in energy than the 4s in ions/compounds. Finally look at the charge on the ion and remove the appropriate number of electrons.

Solution

Co has the ground state electronic configuration $[\text{Ar}] 4s^2 3d^7$.

In a compound, the electronic configuration for $\text{Co}(0)$ is $[\text{Ar}] 3d^9$.

In Co^{2+} , there are two less electrons, so the electronic configuration for Co^{2+} is $[\text{Ar}] 3d^7$.

In Co^+ , there is one less electron, so the electronic configuration for Co^+ is $[\text{Ar}] 3d^8$.

WE 28.3 Naming coordination compounds

- What is the name of the compound $[\text{CoI}_2(\text{en})_2]\text{I}$?
- What is the formula of the compound diaquadibromodi(methylamine)cobalt(III) nitrate?

Strategy

Use the rules given on pages 1261-1262 to determine the name/formula of the two compounds.

Solution

- (a) $[\text{CoI}_2(\text{en})_2]\text{I}$ is bis(ethane-1,2-diamine)diiodocobalt(III) iodide. (*Note:* ethane 1,2-diamine is often called ethylenediamine.)
- (b) The formula of diaquadibromodi(methylamine)cobalt(III) nitrate is $[\text{CoBr}_2(\text{H}_2\text{O})_2(\text{MeNH}_2)_2]\text{NO}_3$.

WE 28.5 High spin or low spin?

For $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, Δ_o is 120 kJ mol^{-1} . Assume Fe^{2+} has the same pairing energy as Cr^{2+} . Calculate the CFSE for the high spin and low spin $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, and predict whether this complex is high spin or low spin.

Strategy

Write down the ground state configuration of iron. Then place all of the 4s electrons into the 3d orbitals if they are available as the 3d orbitals are lower in energy than the 4s in ions/compounds. Then look at the charge on the ion and remove the appropriate number of electrons. Draw out the electronic configuration of the high spin and low spin complexes using Table 28.7 (p.1276). Each electron in a t_{2g} orbital contributes $-0.4\Delta_o$, and each electron in an e_g orbital contributes $+0.6\Delta_o$ to the CFSE.

Solution

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is an octahedral complex of iron (Fe). The ground state electronic configuration of the iron atom is $[\text{Ar}] 4s^2 3d^6$. Moving all the s electrons into the d orbital to give the configuration of a neutral Fe atom in a complex gives $[\text{Ar}] 3d^8$. The charge on the complex is 2+, so the configuration of the iron ion is $3d^6$.

From Table 28.7 (p.1276), $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is a d^6 octahedral complex.

For high spin Fe^{2+} , $\text{CFSE} = -0.4\Delta_o = -0.4 \times 120 \text{ kJ mol}^{-1} = -48 \text{ kJ mol}^{-1}$

For low spin Fe^{2+} , $\text{CFSE} = -2.4\Delta_o + 2P = (-2.4 \times 120 \text{ kJ mol}^{-1}) + (2 \times 245 \text{ kJ mol}^{-1})$
 $= +202 \text{ kJ mol}^{-1}$

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is high spin, as this is the more stable form.

WE 28.7 Magnetic moments

The magnetic moment of $\text{K}_3[\text{Fe}(\text{ox})_3]$ is measured to be $5.95 \mu\text{B}$. Is the complex high spin or low spin?

Strategy

This problem can be solved using two methods. The mathematical way involves rearranging Equation 28.2, $\mu_{\text{SO}} = \sqrt{n(n+2)}$ where n is the number of unpaired electrons and solving for n . The second method uses trial and error to compare the results of this equation for the two possible configurations.

Solution

Firstly, the mathematical method.

Squaring both sides of Equation 28.2 gives

$$(5.95)^2 = n(n + 2)$$

Note that the square of the magnetic moment must be given to the nearest integer.

This gives the quadratic equation

$$35 = n^2 + 2n, \text{ which rearranges to } n^2 + 2n - 35 = 0$$

Factorising gives

$$(n + 7)(n - 5) = 0$$

As n must be a positive integer, the only allowed value is $n = 5$. Therefore the complex has five unpaired electrons. As shown in Table 28.7 (p.1276), this means the complex must be high spin d^5 .

The non mathematical way to solve this problem uses trial and error for the two possible configurations. $[\text{Fe}(\text{ox})_3]^{3-}$ is an iron(III) complex, so it has the electronic configuration d^5 . From Table 28.7, the high spin complex has five unpaired electrons, so

$$\mu_{\text{SO}} = \sqrt{5 \times 7} = \sqrt{35} = 5.92$$

The low spin complex has one unpaired electron, so

$$\mu_{\text{so}} = \sqrt{1 \times 3} = \sqrt{3} = 1.73$$

The measured value is closer to the high spin value, so $\text{K}_3[\text{Fe}(\text{ox})_3]$ is a high spin complex.

Answers to boxes

Box 28.1 Technetium and imaging the brain

Some technetium compounds take several steps to prepare from the pertechnetate obtained from the 'technetium cow'. Suggest why such compounds are unsuitable for use as imaging agent.

Strategy

Consider why technetium is such a useful imaging agent and how it is used.

Solution

The half life of $^{99\text{m}}\text{Tc}$ is only 6 hours making it a useful imaging agent as the effect on the patient is short-lived. However, if the compound cannot be made quickly from the pertechnetate that is obtained from the 'technetium cow', it will have mostly decayed before being used.

Box 28.5 Ferromagnetism and recording information

The structure of Fe_2O_3 consists of a hexagonal close-packed array of oxide ions, with the iron ions in some of the octahedral sites. Given that oxide is a weak field ligand, determine the occupation of the t_{2g} and e_g orbitals.

Strategy

Write down the ground state configuration of iron. Then place all of the 4s electrons into the 3d orbitals as the 3d orbitals are lower in energy than the 4s in the transition metal compounds. Determine the charge on the iron by carrying out a charge balance equation for the oxide ions and remove the appropriate number of electrons from the 3d orbital. Finally, draw out the electronic configuration of the high spin complex as

the electron promotion energy will be lower than the pairing energy for a weak field ligand.

Solution

In ferric oxide, iron is in the 3+ oxidation state. Iron(III) has the electronic configuration $[\text{Ar}] 3d^5$. In an octahedral environment, with a weak field ligand, the occupation of the d orbitals is $(t_{2g})^3 (e_g)^2$.

Box 28.7 Haemoglobin and the transport of oxygen

Attempts to make artificial blood using simple iron–porphyrin compounds, without the protein chain, fail because the resulting oxygen compounds, dimerize with each O_2 molecule binding to two iron atoms. Suggest how this dimerization could be avoided.

Strategy

Consider ways to prevent the O_2 molecules binding to more than one iron centre.

Solution

Bulky groups are added to the porphyrin rings to prevent them from getting close enough for the O_2 molecules to bridge between the porphyrin rings and give dimers.

Answers to end of chapter questions

1. Give the electronic configuration for the following atoms and ions: (a) V^{3+} ; (b) Fe; (c) Cr; (d) Ag^+ ; (e) Fe(0) (in $[\text{Fe}(\text{CO})_5]$); (f) Cu^{2+} ; (g) Ru^{2+} ; (h) W^{4+} .

Strategy

Write down the ground state configuration for the transition metal atom. Then place all of the $4s$ electrons into the $3d$ orbitals if they are available as the $3d$ orbitals are lower in energy than the $4s$ in ions/compounds. Finally look at the charge on the ion and remove the appropriate number of electrons.

Solution

(a) V^{3+} : $[\text{Ar}] 3d^2$

- (b) Fe: $[\text{Ar}] 3d^6 4s^2$
- (c) Cr: $[\text{Ar}] 3d^5 4s^1$
- (d) Ag^+ $[\text{Kr}] 4d^{10}$
- (e) Fe(0): $[\text{Ar}] 3d^8$ (in a compound the $3d$ orbitals are lower in energy than the $4s$ orbital)
- (f) Cu^{2+} : $[\text{Ar}] 3d^9$
- (g) Ru^{2+} : $[\text{Kr}] 4d^6$
- (h) W^{4+} : $[\text{Xe}] 4f^{14} 5d^2$

3. Name the following coordination compounds; (a) $[\text{Ni}(\text{NH}_3)_5]\text{NO}_3$; (b) $\text{K}[\text{Co}(\text{ox})_2(\text{H}_2\text{O})_2]$; (c) $[\text{Fe}(\text{dien})_2]\text{SO}_4$; (d) $\text{Na}[\text{AuBr}_2\text{Cl}_2]$.

Strategy

Use the rules given on pages 1261-1262 to determine the name of the compounds.

Solution

- (a) Pentaammineiodonickel(II) nitrate
- (b) Potassium diaquadioxalatocobaltate(III)
- (c) Bis(1,4,7-triazaheptane)iron(II) sulfate
- (d) Sodium dibromodichloroaurate(III). (*Note:* The name change from gold to aurate for the anionic compound.)

5. Which of the following pairs of compounds are isomers? Explain your reasoning and name the type of any isomerism present.

- (a) $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$
- (b) $[\text{CoCl}(\text{NH}_3)_5]\text{SeO}_4$ and $[\text{Co}(\text{SeO}_4)(\text{NH}_3)_5]\text{Cl}$
- (c) $[\text{Pt}(\text{NH}_3)_4][\text{PtBr}_4]$ and $[\text{PtBr}(\text{NH}_3)_3][\text{PtBr}_3(\text{NH}_3)]$
- (d) $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$ and $[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2$

Strategy

Isomers must have the same chemical formula but differ in the arrangement of the atoms. Use Figure 28.16 (p.1263) and the descriptions on the following pages to

determine whether the pairs of compounds are isomers and, if so, what type of isomerism is present.

Solution

- (a) No. These are not isomers, as the number of potassium ions differs.
- (b) Yes. These are ionization isomers. The compounds have the same empirical formula, but differ in terms in which ligands are coordinated.
- (c) Yes. These are coordination isomers. The compounds have the same empirical formula, but differ in which ligands are coordinated to each metal.
- (d) Yes. These are linkage isomers. The nitrite is an ambidentate ligand.

7. Dimethylsulfoxide (DMSO, Me₂SO) is an ambidentate ligand as it can act as a *S*-donor or an *O*-donor.

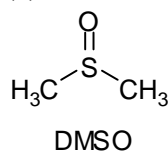
- (a) Use VSEPR theory to show there is a lone pair on the sulfur atom.
- (b) Use the hard and soft acids and bases theory to predict which atom will coordinate to (i) Pt²⁺ and (ii) Fe³⁺.

Strategy

Use VSEPR theory to determine the structure around the sulfur where the Me groups act as one electron donors and the oxygen as a two electron donor forming a double bond. (VSEPR theory is described in Section 4.2, p.183.) In part (b), consider the charge and underlying structure of the cation to determine whether it is likely to bond to oxygen (hard base) or sulfur (soft base).

Solution

(a)

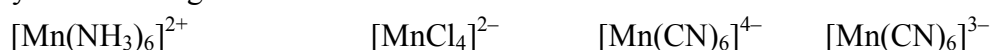


Electrons from S	6
Electrons from two Me groups	2
Electrons from O	2
Total no. electrons around S	10
Five electron pairs around S, but one is a π -pair	

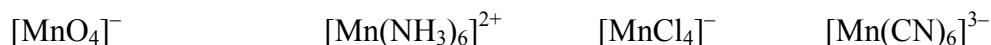
Four σ -electron pairs, so three bonding pairs and one lone pair.

- (b) (i) Pt^{2+} is a soft metal so likely to form more stable complexes with the softer *S*-donor.
 (ii) Fe^{3+} is a hard metal so likely to form more stable complexes with the harder *O*-donor.

9. (a) Rank the following manganese complexes in order of increasing Δ . Explain your reasoning.



- (b) Rank the following manganese complexes in order of increasing intensity of colour. Explain your reasoning.

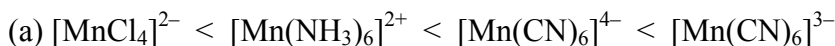


Strategy

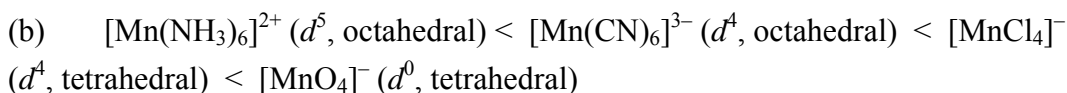
(a) Δ_o increases with the position of the ligand in the spectrochemical series. Weak field ligands such as chloride with full *p* orbitals are σ donor, π donor ligands lie low in the spectrochemical series whereas strong field ligands such as cyanide are σ donor, π acceptor ligands and lie at the high end of the series.

(b) The intensity of the transitions are dependent on a number of selection rules. The strongest colour will be achieved for complexes which break none of these rules such as charge transfer reactions where $\Delta l = +/ - 1$. For transitions within the orbitals of the same secondary quantum number, first parity and then spin multiplicity must be considered.

Solution



$\Delta_t < \Delta_o$, so $[\text{MnCl}_4]^{2-}$ is lowest. $[\text{Mn}(\text{NH}_3)_6]^{2+}$ and $[\text{Mn}(\text{CN})_6]^{4-}$ are both Mn(II) complexes, but CN^- is higher in the spectrochemical series than NH_3 . $[\text{Mn}(\text{CN})_6]^{3-}$ is a Mn(III) complex, so Δ_o will be higher than for the Mn(II) complexes.



The transitions in $[\text{Mn}(\text{NH}_3)_6]^{2+}$ break the spin, Laporte and parity selection rules. Those in $[\text{Mn}(\text{CN})_6]^{3-}$ break the Laporte and parity selection rules, and those in $[\text{MnCl}_4]^-$ break only the Laporte selection rule. The transitions in $[\text{MnO}_4]^-$ are charge-transfer bands so break none of the selection rules.

11. Write down expressions for the crystal field stabilization energy (CFSE) for a high spin and low spin d^4 complex in terms of Δ_o and P , the pairing energy. Use these expressions together with the data below to predict whether $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Re}(\text{H}_2\text{O})_6]^{3+}$ form high spin or low spin complexes.

	$\Delta_o / \text{kJ mol}^{-1}$	$P / \text{kJ mol}^{-1}$
$[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$	250	300
$[\text{Re}(\text{H}_2\text{O})_6]^{3+}$	400	180

Strategy

Draw diagrams for the high spin and low spin configurations of d^4 and write down an expression for the CFSE (remember to including the pairing energy in the low spin configuration). Use the values given in the table to calculate which configuration is most favoured.

Solution

From Table 28.7 (p.1276),

For $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$:

$$\text{CFSE for } d^4 \text{ high spin} = -0.6 \times 250 \text{ kJ mol}^{-1} = -150 \text{ kJ mol}^{-1}$$

$$\text{CFSE for } d^4 \text{ low spin} = -1.6 \times 250 \text{ kJ mol}^{-1} + 300 \text{ kJ mol}^{-1} = -100 \text{ kJ mol}^{-1}$$

So $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ is a high spin complex (this is more stable).

For $[\text{Re}(\text{H}_2\text{O})_6]^{3+}$:

$$\text{CFSE for } d^4 \text{ high spin} = -0.6 \times 400 \text{ kJ mol}^{-1} = -240 \text{ kJ mol}^{-1}$$

$$\text{CFSE for } d^4 \text{ low spin} = -1.6 \times 400 \text{ kJ mol}^{-1} + 180 \text{ kJ mol}^{-1} = -460 \text{ kJ mol}^{-1}$$

So $[\text{Re}(\text{H}_2\text{O})_6]^{3+}$ is a low spin complex (this is more stable).

Note for the heavier *4d* and *5d* transition metals that the crystal field splitting is large compared with the pairing energy and hence the low spin configuration is always favoured.

- 13.** Use the spin-only formula (Equation 28.2, p.1283) to predict the magnetic moments of the following compounds: (a) $[\text{Ni}(\text{en})_3]\text{SO}_4$; (b) $\text{Na}_2[\text{CoCl}_4]$; (c) *trans*- $[\text{MnF}_2(\text{NH}_3)_4]$; (d) $\text{K}_2[\text{Cr}_2\text{O}_7]$.

Strategy

Equation 28.2 gives $\mu_{\text{so}} = \sqrt{n(n+2)}$ where n is the number of unpaired electrons.

Therefore by working out the number of unpaired electrons by drawing out the electronic configuration, the magnetic moment can be calculated.

Solution

(a) This is a nickel(II) complex so d^8 octahedral. There are two unpaired electrons so using Equation 28.2,

$$\mu_{\text{so}} = \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \mu_{\text{B}}$$

(b) This is a cobalt(II) complex so d^7 tetrahedral. There are three unpaired electrons:

$$\mu_{\text{so}} = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \mu_{\text{B}}$$

(c) This is a manganese(II) complex so d^5 octahedral. There are five unpaired electrons:

$$\mu_{\text{so}} = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \mu_{\text{B}}$$

(d) This is a chromium(VII) complex, so it has no d electrons. $\mu_{\text{so}} = 0 \mu_{\text{B}}$ (it is diamagnetic).

15. An amateur chemist believes he has discovered a new *d*-block element, bloggrium (Bg). Bloggrium forms a chloride that is a liquid at room temperature. This compound fumes in moist air and is hydrolysed to an oxide which contains 59.9% bloggrium. The UV-visible spectrum of Bg^{3+} (aq) contains a single broad absorbance, and this solution is oxidized on contact with air. Suggest a known element that fits this description, and write out balanced equations for the reactions.

Strategy

Use the information given in this chapter on p 1253, 1254 and 1280 to identify bloggrium. Of particular interest is the instability of the metal halide as most transition metal halides are very stable materials. Also consider why the metal halide bonds are hydrolysed, suggesting that Bg–O is strong compared to Bg–X. Finally the UV spectrum for Bg^{3+} consists of a broad UV absorption which must correspond to a *d*–*d* transition of some sort. As the narrative also adds the bloggrium cation is further oxidised on exposure to air, bloggrium must have at least one oxidation state greater than 3+.

Solution

As more electrons can be removed from Bg^{3+} as it can be further oxidised, bloggrium must have at least one more accessible oxidation state. From Table 28.7 (p.1276), this means that the transition metal must lie in one of the groups headed by Ti to Co.

However, most of the chlorides within these groups are very stable solid materials except titanium (IV) chloride (see Section 28.2 on halides on p.1254) which is easily hydrolysed in air to form TiO_2 . This factor would strongly suggest that bloggrium is in fact titanium.

This is proven by the fact that TiO_2 , is 59.9% titanium and 40.1% oxygen by mass as indicated in the question.

As Ti^{3+} has the electronic configuration $[\text{Ar}] 3d^1$, and the absorbance in the UV-visible spectrum arises from the electronic transition $t_{2g} \rightarrow e_g$. Ti^{3+} is oxidized by oxygen in the air to form TiO^{2+} .

