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## *d*-Block chemistry

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### Answers to worked examples

**WE 28.1 Electronic configurations (on p. 1259 in *Chemistry*<sup>3</sup>)**

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

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

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

**WE 28.2 Oxidation states in coordination complexes (on p. 1268 in *Chemistry*<sup>3</sup>)**

What is the oxidation state of vanadium in the complex  $[\text{VO}(\text{acac})_2]$ ? (See Table 28.4 (p.1267 for the structure of the acac ligand.)

Strategy

Determine the charge of the individual ligands and assume the charge on the cation exactly balances this charge as the complex is neutral.

Solution

The acac ligands each carry a  $-1$  charge, and the oxo ligand carries a  $-2$  charge, so the total ligand charge is  $-4$ . The complex is neutral, so the vanadium oxidation state is  $+4$ .

**WE 28.3 Naming coordination compounds (on p. 1272 in *Chemistry*<sup>3</sup>)**

- 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 1270-2 to determine the name/formula of the two compounds.

Solution

- $[\text{CoI}_2(\text{en})_2]\text{I}$  is bis(ethane-1,2-diamine)diodocobalt(III) iodide. (*Note:* ethane 1,2-diamine is often called ethylenediamine.)
- 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 28.4 Crystal field stabilization energy (on p. 1283 in *Chemistry*<sup>3</sup>)**

Calculate the crystal field stabilisation energy for  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ .

Strategy

Write down the ground state configuration of chromium. 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. Place the electrons into the lowest energy orbitals, obeying Hund's rule. 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

$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  is an octahedral complex of chromium (Cr). The ground state electronic configuration of the chromium atom is  $[\text{Ar}] 4s^1 3d^5$ . Moving all the  $s$  electrons into the  $d$  orbitals to give the configuration of a neutral Cr atom in a complex gives  $[\text{Ar}] 3d^6$ .

The charge on the complex is 3+, so the configuration of the Cr ion is  $3d^3$ .

Placing the electrons in the crystal field splitting diagram for an octahedral complex given in Figure 28.29 according to Hund's rule gives three electrons in the  $t_{2g}$  orbitals.

$$\text{The CFSE} = 3 \times (-0.4\Delta_o) + 0 \times (+0.6\Delta_o) = -1.2\Delta_o.$$

**WE 28.5 High spin or low spin? (on p. 1286 in *Chemistry*<sup>3</sup>)**

For  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  $\Delta_o$  is 120  $\text{kJ mol}^{-1}$ . Assume  $\text{Fe}^{2+}$  has the same pairing energy as  $\text{Cr}^{2+}$ . 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.1285). 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  $d$  orbitals 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.1285),  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  is a  $d^6$  octahedral complex.

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

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

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

### WE 28.6 The Jahn–Teller effect (on p. 1288 in *Chemistry*<sup>3</sup>)

Would you predict a Jahn–Teller distortion to be observed for  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ?

#### Strategy

Determine the oxidation state of manganese in the complex and write down the valence electronic configuration of the manganese ion. Use the factors given on p.1284 to decide whether the complex is likely to be low or high spin. If there is more than one way to arrange the electrons while still obeying Hund's rule, the complex will undergo a Jahn–Teller distortion to remove the degeneracy and lower the energy of the system.

#### Solution

Neutral manganese in a complex has an electronic configuration of  $[\text{Ar}] 3d^7$ . Therefore the 2+ cation has the configuration  $[\text{Ar}] 3d^5$  as two electrons have been lost.

$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  is a high spin octahedral complex for the same reason as  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  in Worked Example 28.6. This gives the  $d$  orbital occupation  $(t_{2g})^3 (e_g)^2$ . There is one electron in each of the  $e_g$  orbitals, so no degeneracy. The complex does not undergo a Jahn–Teller distortion.

### WE 28.7 Magnetic moments (on p. 1293 in *Chemistry*<sup>3</sup>)

The magnetic moment of  $\text{K}_3[\text{Fe}(\text{ox})_3]$  is measured to be  $5.95 \mu\text{B}$ . Is this a high spin or a low spin complex? (ox = ethanedionato. See Table 28.4, p.1267.)

#### Strategy

This problem can be solved using two methods. The mathematical way involves rearranging Equation 28.2,  $m_{\text{SO}} = \sqrt{n(n+2)}$ , 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.1285), this means the complex must be high spin  $d^5$ .

The other 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

$$m_{\text{so}} = \sqrt{5 \times 7} = \sqrt{35} = 5.92$$

The low spin complex has one unpaired electron, so

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

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 (on p. 1257 in *Chemistry*<sup>3</sup>)

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 agents.

#### Strategy

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

#### Solution

The half life of <sup>99m</sup>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 28.2 The extraction of gold (on p. 1268 in *Chemistry*<sup>3</sup>)

What is the oxidation state of gold in the  $[\text{Au}(\text{CN})_2]^-$  complex? What shape would you predict for this complex ion?

#### Strategy

Determine the charge of the individual ligands and assume the charge on the gold cation is the difference between the sum of these charges and the charge on the complex. The coordination number gives the shape shown in Section 28.3 (p.1268).

#### Solution

Cyanide has a negative charge ( $\text{CN}^-$ ), so  $[\text{Au}(\text{CN})_2]^-$  is a gold(I) complex. It is two-coordinate, so linear in shape.

### Box 28.3 Platinum anti-cancer drugs (on p. 1275 in *Chemistry*<sup>3</sup>)

What are the systematic names for *cis*-platin and satraplatin? (Ignore the stereochemistry for satraplatin.)

Strategy

Look at the rules for naming coordination compounds in Section 28.3 (p. 1270-2).

Solution

In the compound name, the ligands are placed in alphabetical order. Thus *cis*-platin is *cis*-diamminedichloroplatinum(II). Satraplatin is one of the isomers of amminedichloro(cyclohexylamine)diethanoatoplatinum(IV).

**Box 28.4 Coordination networks (on p. 1278 in *Chemistry*<sup>3</sup>)**

What is the formula of the network structure formed when ethanoato ligands in structure (15) are replaced by 1,4-benzenedicarboxylato ligands?

Strategy

Determine the number of ethanoato ligands that will be replaced by the 1,4-benzenedicarboxylato ligand by considering the number of carboxylate groups on each ligand.

Solution

Each 1,4-benzenedicarboxylate substitutes for two acetates, one on each of two separate  $Zn_4O$  units. The formula of the network structure is therefore  $[Zn_4O(O_2CC_6H_4CO_2)_3]$ .

**Box 28.5 Ferromagnetism and recording information (on p. 1293 in *Chemistry*<sup>3</sup>)**

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 on the iron centres.

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  $\text{Fe}_2\text{O}_3$ , 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 28.6 Trapping metal ions using the chelate effect (on p. 1296 in *Chemistry*<sup>3</sup>)**

Suggest how titrations with  $\text{Na}_4[\text{EDTA}]$  could be used in the quantitative analysis of metal ions.

Strategy

The chelating effect of EDTA is extremely strong (as it is a hexadentate ligand). Consider how this property affects the metal/ligand equilibrium reaction.

Solution

A solution of metal ions of unknown concentration can be titrated with a solution of  $\text{Na}_4[\text{edta}]$  of known concentration. The equilibrium constants for reactions of metal ions with  $\text{edta}^{4-}$  are so high that the reactions essentially go to completion.

**Box 28.7 Haemoglobin and the transport of oxygen (on p. 1298 in *Chemistry*<sup>3</sup>)**

Attempts to make artificial blood using simple iron–porphyrin compounds, without the protein chain, fail because the resulting oxygen compounds, dimerize with each  $\text{O}_2$  molecule binding to two iron atoms. Suggest how this dimerization could be avoided.

Strategy

Consider ways to prevent the  $\text{O}_2$  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  $\text{O}_2$  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  $[Fe(CO)_5]$ ); (f)  $Cu^{2+}$ ; (g)  $Ru^{2+}$ ; (h)  $W^{4+}$ .

### Strategy

Write down the ground state configuration for the transition metal atom. Then, for the ions and the complex, 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)  $V^{3+}$ :  $[Ar] 3d^2$   
(b) Fe:  $[Ar] 3d^6 4s^2$   
(c) Cr:  $[Ar] 3d^5 4s^1$   
(d)  $Ag^+$   $[Kr] 4d^{10}$   
(e) Fe(0):  $[Ar] 3d^8$  (in a compound the 3d orbitals are lower in energy than the 4s orbital)  
(f)  $Cu^{2+}$ :  $[Ar] 3d^9$   
(g)  $Ru^{2+}$ :  $[Kr] 4d^6$   
(h)  $W^{4+}$ :  $[Xe] 4f^{14} 5d^2$

2. Explain why the +3 oxidation state becomes increasingly less stable with respect to the +2 oxidation state on moving from left to right across the first row of the d-block elements.

### Strategy

Consider the atomic parameters that contribute to the relative stabilities of oxidation states, and how these are affected by the change in  $Z_{\text{eff}}$  expected on moving from left to right across the d-block elements.

### Solution

The variations in oxidation state stability are due to the increase in third ionization energy across the row (Figure 28.4, p.1261). As the third ionization energy increases, it becomes energetically less favourable to form the +3 oxidation state. The ionization

energy increases due to the increase in  $Z_{\text{eff}}$ , itself a consequence of the inefficient shielding provided by the  $d$  electrons.

3. Give the oxidation state and coordination number of the metal in the following complexes: (a)  $[\text{Cr}(\text{CN})_6]^{3-}$ ; (b)  $[\text{PdCl}_2(\text{PBU}_3)_2]$ ; (c)  $[\text{VO}(\text{acac})_2]$ ; (d)  $[\text{Ru}(\text{terpy})_2]^{2+}$ ; (e)  $[\text{Cr}(\text{ox})_3]^{3-}$ .

### Strategy

Determine the charge of the individual ligands and assume the charge on the cation is the difference between this number and the charge on the complex. To work out the coordination number is just a matter of counting up the ligands and taking into account the denticity of the ligands.

### Solution

- (a) Each cyano ligand is monoanionic ( $\text{CN}^-$ ). As the total charge on the complex is  $-3$  the chromium oxidation state must be  $+3$ . The cyano ligands are all monodentate, so the coordination number is 6.
- (b) The chloro ligand is monoanionic and  $\text{PPh}_3$  is neutral. Since the complex is neutral, the palladium oxidation state is  $+2$ . All of the ligands are monodentate, so the coordination number is 4.
- (c) The oxo ligand is dianionic ( $\text{O}^{2-}$ ), and each  $\text{acac}^-$  ligand is monoanionic. Since the complex is neutral, the vanadium oxidation state is  $+4$ . The oxo ligand is monodentate, whereas  $\text{acac}^-$  is bidentate. The coordination number is 5.
- (d) The terpy ligands are neutral, so the ruthenium oxidation state is the same as the charge on the complex, which is  $+2$ . Each terpy ligand is tridentate, so the coordination number is 6.
- (e) Each oxalate ligand is dianionic. As the total charge on the complex is  $-3$  the chromium oxidation state must be  $+3$ . The oxalate ligands are all bidentate, so the coordination number is 6.

4. 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 1270-2 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 changes from gold to aurate for the anionic compound.)

5. Determine the formulae of the following coordination compounds:

- (a) chloro(diethylsulfide)gold(I);  
(b) tetraethylammonium tetrabromoferrate(III);  
(c) bis(2,2'-bipyridine)dicarbonylmolybdenum(0);  
(d) potassium hexanitrito- $\kappa O$ -cobaltate(III).

Strategy

Use the rules given on pages 1270-2 to determine the formulae of the compounds.

Solution

- (a)  $[\text{AuCl}(\text{SEt}_2)]$   
(b)  $[\text{NEt}_4][\text{FeBr}_4]$   
(c)  $[\text{Mo}(\text{bipy})_2(\text{CO})_2]$   
(d)  $\text{K}_3[\text{Co}(\text{ONO})_6]$

6. Compounds X and Y have the same molecular formula and contain 18.25% titanium, 40.54% chlorine, 36.59% oxygen, and 4.61% hydrogen. When 0.5000 g of X was dissolved in water and treated with silver nitrate solution, 0.2731 g of silver chloride were precipitated. 0.5000 g of Y were dissolved in water and titrated against 0.2000 mol dm<sup>-3</sup> silver nitrate solution, of which 28.2 cm<sup>3</sup> were required. Identify X and Y, and determine any possible isomers.

Strategy

First calculate the empirical formula by calculating the molar ratios (divide % by Ar) and dividing the smallest into the others. Assume O and H are present as water molecules. Next determine how the halides are coordinated by using the titre to calculate the number of moles of halide per mole of complex

Solution

	<b>Ti</b>	<b>Cl</b>	<b>O</b>	<b>H</b>
% mass	18.25	40.54	36.59	4.61
mass in g	18.25 g	40.54 g	36.59 g	4.61 g
amount (in mol)	$\frac{18.25 \text{ g}}{47.867 \text{ g mol}^{-1}}$	$\frac{40.54 \text{ g}}{35.453 \text{ g mol}^{-1}}$	$\frac{36.59 \text{ g}}{15.999 \text{ g mol}^{-1}}$	$\frac{4.61 \text{ g}}{1.0079 \text{ g mol}^{-1}}$
	= 0.3813 mol	= 1.143 mol	= 2.287 mol	= 4.574 mol
simplest ratio (divide by smallest)	$\frac{0.3813 \text{ mol}}{0.3813 \text{ mol}}$	$\frac{1.143 \text{ mol}}{0.3813 \text{ mol}}$	$\frac{2.287 \text{ mol}}{0.3813 \text{ mol}}$	$\frac{4.574 \text{ mol}}{0.3813 \text{ mol}}$
	= 1	= 3	= 6	= 12

Empirical formula is  $\text{TiCl}_3\text{O}_6\text{H}_{12}$ , but assuming the H and O are combined as water, this is written as  $\text{TiCl}_3(\text{H}_2\text{O})_6$ . This formula gives the ions in the molecular formula but not how these ions are bonded to the central transition metal. As titanium is a first row transition metal, the most likely coordination number is 6, therefore three of the nine ligands/anions are not directly bonded to the Ti centre.

On titration with silver nitrate, only the counter anions will react as those that are connected to the titanium will not be released into solution.

$$0.5000 \text{ g of X contain } \frac{0.5000 \text{ g}}{262.3 \text{ g mol}^{-1}} = 1.91 \times 10^{-3} \text{ mol}$$

$$0.2731 \text{ g of AgCl contain } \frac{0.2731 \text{ g}}{143.3 \text{ g mol}^{-1}} = 1.91 \times 10^{-3} \text{ mol}$$

$1.91 \times 10^{-3} \text{ mol AgCl}$  are precipitated from  $1.91 \times 10^{-3} \text{ mol X}$

So, 1 mol X contains 1 mol uncoordinated  $\text{Cl}^-$  ions.

X is  $[\text{TiCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ . Geometric *cis* and *trans* isomers of X are possible.

**Y** reacts with exactly 28.2 cm<sup>3</sup> of 0.2000 mol dm<sup>-3</sup> silver nitrate solution.

$$28.2 \text{ cm}^3 \text{ of } 0.2000 \text{ mol dm}^{-3} \text{ silver nitrate solution contain } \frac{28.2}{1000} \text{ dm}^3 \times 0.20 \text{ mol dm}^{-3} \\ = 5.64 \times 10^{-3} \text{ mol}$$

$1.91 \times 10^{-3}$  mol **Y** contain  $5.64 \times 10^{-3}$  mol uncoordinated Cl<sup>-</sup> ions.

1 mol **Y** contains 3 mol uncoordinated Cl<sup>-</sup> ions.

**Y** is [Ti(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub>. No isomers of **Y** are possible.

7. Which of the following pairs of compounds are isomers? Explain your reasoning and name the type of any isomerism present.
- K<sub>3</sub>[Fe(CN)<sub>6</sub>] and K<sub>4</sub>[Fe(CN)<sub>6</sub>]
  - [CoCl(NH<sub>3</sub>)<sub>5</sub>]SeO<sub>4</sub> and [Co(SeO<sub>4</sub>)(NH<sub>3</sub>)<sub>5</sub>]Cl
  - [Pt(NH<sub>3</sub>)<sub>4</sub>][PtBr<sub>4</sub>] and [PtBr(NH<sub>3</sub>)<sub>3</sub>][PtBr<sub>3</sub>(NH<sub>3</sub>)]
  - [Co(NO<sub>2</sub>)(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>2</sub> and [Co(ONO)(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>2</sub>

#### Strategy

Isomers must have the same chemical formula but differ in the arrangement of the atoms. Use Figure 28.15 (p.1272) 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

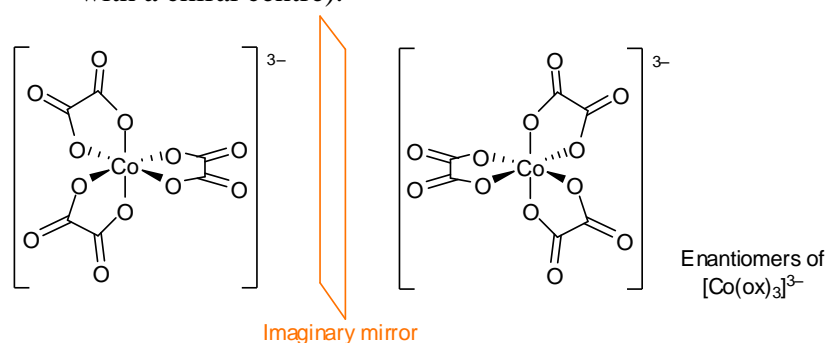
- No. These are not isomers, as the number of potassium ions differs.
  - Yes. These are ionization isomers. The compounds have the same empirical formula, but differ in terms in which ligands are coordinated.
  - Yes. These are coordination isomers. The compounds have the same empirical formula, but differ in which ligands are coordinated to each metal.
  - Yes. These are linkage isomers. The nitrite ion is an ambidentate ligand.
8. Sketch the possible isomers for the following compounds and identify the type of isomerism involved: (a) [Co(ox)<sub>3</sub>]<sup>3-</sup>; (b) [NiCl<sub>2</sub>(en)<sub>2</sub>]; (c) [NiCl<sub>2</sub>(py)<sub>2</sub>]; (d) [FeF<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>].

Strategy

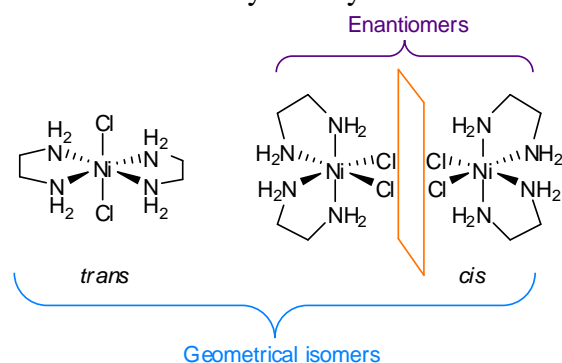
Draw out the possible isomers being careful to consider the effect of multidentate ligands. This type of question really benefits from using a molecular model kit to illustrate the spatial arrangement of the atoms.

Solution

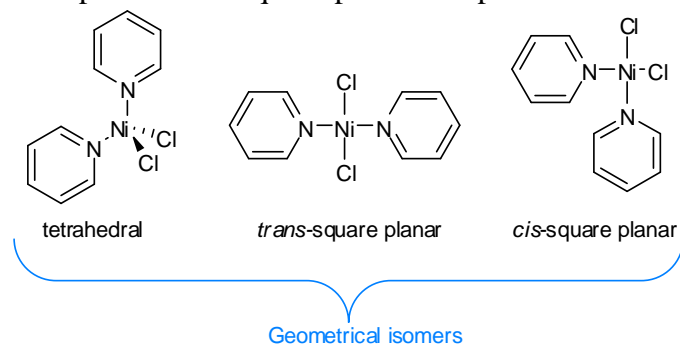
- (a)  $[\text{Co}(\text{ox})_3]^{3-}$  has no plane or centre of symmetry and forms enantiomers (isomers with a chiral centre).



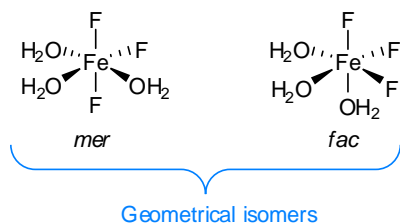
- (b)  $[\text{NiCl}_2(\text{en})_2]$  forms geometrical isomers. In addition, the *cis* isomer has no plane or centre of symmetry and forms enantiomers.



- (c)  $[\text{NiCl}_2(\text{py})_2]$  is four-coordinate so the geometry is either tetrahedral or square-planar. The square-planar compound forms *cis* and *trans* geometrical isomers.



- (d)  $[\text{FeF}_3(\text{H}_2\text{O})_3]$  forms *fac* and *mer* geometrical isomers.



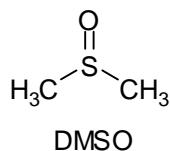
9. Dimethylsulfoxide (DMSO,  $\text{Me}_2\text{SO}$ ) is an ambidentate ligand as it can act as a *S*-donor or an *O*-donor.
- (a) Use VSEPR theory to show there is a lone pair on the sulfur atom.
- (b) Use the hard and soft acids and bases theory to predict which atom will coordinate to (i)  $\text{Pt}^{2+}$  and (ii)  $\text{Fe}^{3+}$ .

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 5.2, p.223.) 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  $\pi$ -pair

Four  $\sigma$ -electron pairs, so three bonding pairs and one lone pair.

- (b) (i)  $\text{Pt}^{2+}$  is a soft metal so likely to form more stable complexes with the softer *S*-donor.

(ii)  $\text{Fe}^{3+}$  is a hard metal so likely to form more stable complexes with the harder *O*-donor.

**10.** For each of the following pairs of complexes, identify which has the higher value of  $\Delta$ . Explain your answers.

- (a)  $[\text{TiCl}_6]^{3-}$  or  $[\text{TiCl}_4]^-$
- (b)  $[\text{NiCl}_4]^{2-}$  or  $[\text{NiBr}_4]^{2-}$
- (c)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  or  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

Strategy

Consider the factors given in Section 28.5 (p.1282) that contribute to  $\Delta$ .

Solution

- (a)  $[\text{TiCl}_6]^{3-}$  has an octahedral geometry whereas  $[\text{TiCl}_4]^-$  has a tetrahedral geometry.  $\Delta_o$  is bigger than  $\Delta_t$ , so  $\Delta$  is greater for  $[\text{TiCl}_6]^{3-}$ .
- (b) Chloride is higher in the spectrochemical series than bromide, so  $\Delta$  is greater for  $[\text{NiCl}_4]^{2-}$ .
- (c)  $\Delta$  increases with increasing charge on the metal atom, so  $\Delta$  is greater for  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ .

**11.** Explaining your reasoning, which of the following complex ions would you expect to be tetragonally distorted?

- (a)  $[\text{Cu}(\text{NH}_3)_6]^{2+}$
- (b)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$
- (c)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
- (d)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

Strategy

Determine the electronic configuration for the metal ion, and work out the occupation of the *d*-orbitals. If there is a degenerate ground state, a tetragonal distortion will occur to remove the degeneracy. This is the Jahn-Teller effect.



Solution

- (a) Copper(II) has an electronic configuration  $[\text{Ar}] 3d^9$ , which in an octahedral complex becomes  $(t_{2g})^6 (e_g)^3$ . The  $e_g$  orbitals are unevenly filled, so a Jahn-Teller distortion occurs.  $[\text{Cu}(\text{NH}_3)_6]^{2+}$  is tetragonally distorted.
- (b) Nickel(II) has an electronic configuration  $[\text{Ar}] 3d^8$ , which in an octahedral complex becomes  $(t_{2g})^6 (e_g)^2$ . The  $e_g$  orbitals each contain one electron, so no Jahn-Teller distortion occurs.  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is not tetragonally distorted.
- (c) Manganese(II) has an electronic configuration  $[\text{Ar}] 3d^5$ , which in a high spin octahedral complex becomes  $(t_{2g})^3 (e_g)^2$ . The  $e_g$  orbitals each contain one electron, so no Jahn-Teller distortion occurs.  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  is not tetragonally distorted.
- (d) Chromium(III) has an electronic configuration  $[\text{Ar}] 3d^3$ , which in an octahedral complex becomes  $(t_{2g})^3 (e_g)^0$ . The  $e_g$  orbitals are both empty, so no Jahn-Teller distortion occurs.  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  is not tetragonally distorted.

12. Write down expressions for the crystal field stabilization energy (CFSE) for a high spin and low spin  $d^4$  complex in terms of  $\Delta_o$  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  $d^4$  configurations 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.1285),

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

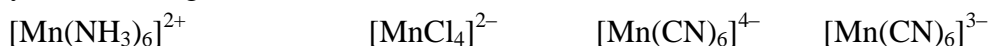
CFSE for  $d^4$  high spin =  $-0.6 \times 400 \text{ kJ mol}^{-1} = -240 \text{ kJ mol}^{-1}$

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

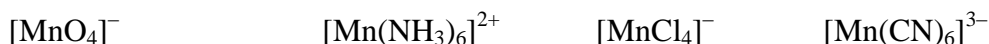
So  $[\text{Re}(\text{H}_2\text{O})_6]^{3+}$  is a low spin complex (this is more stable).

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. (a) Rank the following manganese complexes in order of increasing  $\Delta$ . Explain your reasoning.



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



### Strategy

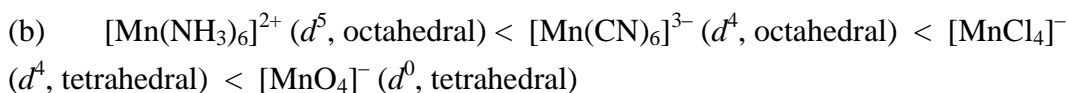
(a)  $\Delta_o$  increases with the position of the ligand in the spectrochemical series. Weak field ligands such as chloride with full  $p$  orbitals are  $\sigma$  donor,  $\pi$  donor ligands so lie low in the spectrochemical series, whereas strong field ligands such as cyanide are  $\sigma$  donor,  $\pi$  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  $\Delta l = \pm 1$ . For transitions within the orbitals of the same secondary quantum number, first parity and then spin multiplicity must be considered.

### Solution

(a)  $[\text{MnCl}_4]^{2-} < [\text{Mn}(\text{NH}_3)_6]^{2+} < [\text{Mn}(\text{CN})_6]^{4-} < [\text{Mn}(\text{CN})_6]^{3-}$

$\Delta_t < \Delta_o$ , 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  $\text{CN}^-$  is higher in the spectrochemical series than  $\text{NH}_3$ .  $[\text{Mn}(\text{CN})_6]^{3-}$  is a Mn(III) complex, so  $\Delta_o$  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.

- 14.** The visible light absorption spectrum for  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  (aq) is shown in Figure 28.35 (p.1290). By considering the nature of the excited state, suggest why the absorption has a shoulder at a higher wavelength than  $\lambda_{\text{max}}$  at 490 nm, suggesting two electronic transitions at slightly different energies.

#### Strategy

As the spectrum indicates two transitions close in energy, it implies that two degenerate orbitals have become non equivalent due to the electronic configuration. It is therefore necessary to determine the electronic configuration of the  $\text{Ti}^{3+}$  cation and draw a crystal field splitting diagram for this cation to investigate why the degeneracy is lost.

#### Solution

The  $\text{Ti}^{3+}$  cation has the configuration  $[\text{Ar}]d^1$ . This means in the ground state the single electron resides in one orbital of the three orbitals in the  $t_{2g}$  set. When the electron is promoted using the UV radiation to the excited state, the electronic configuration is  $(e_g)^1$ . The  $e_g$  orbitals are unevenly filled, so a Jahn–Teller distortion occurs in the excited state. As a result of this, the two  $e_g$  orbitals are no longer degenerate, and the transitions to the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals occur at slightly different wavelengths so two overlapping bands are observed in the UV spectrum.

15. Copper(II) complexes are coloured but copper(I) complexes are generally colourless. Why is this?

Strategy

Transition metal complexes are coloured as transitions between partially filled  $d$  orbitals occur within the visible region. Transitions can only occur if there is a vacancy into which electrons can be promoted.

Solution

Copper(II) has the electronic configuration  $[\text{Ar}] 3d^9$ , so  $d-d$  transitions are possible. These give rise to the colour. Copper(I) has the electronic configuration  $[\text{Ar}] 3d^{10}$ , so  $d-d$  transitions are not possible, hence copper(I) compounds are usually colourless.

16.  $\text{Na}_2[\text{Ni}(\text{CN})_4]$  is diamagnetic not paramagnetic. Use this information to determine the geometry of the anion.

Strategy

The nickel has four-fold geometry and could be either tetrahedral or square planar in shape (see p.1269). Drawing out the two possible electron configurations (see Section 28.4, p.1279) allows the number of unpaired electrons to be calculated. As the complex is diamagnetic, it must have no unpaired electrons.

Solution

$\text{Na}_2[\text{Ni}(\text{CN})_4]$  is a nickel(II) complex so has the electronic configuration  $[\text{Ar}] 3d^8$ . It is four-coordinate, so could be tetrahedral or square planar. A tetrahedral  $d^8$  complex has two unpaired electrons and is paramagnetic. In the square planar geometry all the electrons are paired and the complex is diamagnetic. This means  $[\text{Ni}(\text{CN})_4]^{2-}$  is square planar.

17. Use the spin-only formula (Equation 28.2, p.1292) 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  $\mu_{\text{so}} = \sqrt{n(n+2)} \mu_{\text{B}}$  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,

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

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

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

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

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

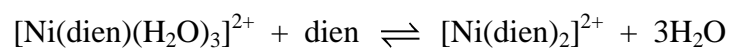
(d) This is a chromium(VI) complex, so it has no  $d$  electrons.  $\mu_{\text{so}} = 0 \mu_{\text{B}}$  (it is diamagnetic).

- 18.** For the reaction between  $\text{Ni}^{2+}(\text{aq})$  and 1,4,7-triazaheptane (dien), the equilibrium constants  $K_1 = 6.5 \times 10^{10}$  and  $K_2 = 1.4 \times 10^8$  have been determined. Write balanced equations for these reactions, and calculate the formation constant  $\beta_2$ .

Strategy

Look at the structure of 1,4,7-triazaheptane (dien) in Table 28.4 (p. 1267) and determine how many water molecules each dien ligand will displace. Starting from  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , work out the products from the reactions, then write out the equations. Remember to balance the water molecules. The formation constant  $\beta_2$  is the product of the stepwise equilibrium constants.

Solution



$$\begin{aligned}\beta_2 &= K_1 K_2 \\ &= (6.5 \times 10^{10}) \times (1.4 \times 10^8) \\ &= 9.1 \times 10^{18}\end{aligned}$$