F325: Equilibria, Energetics and Elements 5.3 Transition Metals

1. transition element: has at least one ion with a partly filled d-orbital (1) (a) (i) example showing electronic configuration with d orbital as between $d^1 - d^9$ (1) complex ion: a central metal ion surrounded by ligands with an example. (1) ligand: molecule/ion with lone pair of electrons capable of forming coordinate/ dative bonds to a metal ion (1) 4 (ii) precipitation: equation (1) colour of precipitate (1) ligand substitution: equation (1) colour of substituted complex (1) redox: equation (1) colour change (1) The candidate clearly links observations to provide evidence for two reactions discussed. (1) 7 (b) complex ions: octahedral example (1) with 3-D diagram (1) tetrahedral example (1) with 3-D diagram (1) square planar example (see also below) (1) with 3-D diagram (1) stereoisomerism: cis-trans example, e.g. Ni(NH₃)₂Cl₂; platin with 3-D diagram (1) optical example, e.g. Ni(en)₃²⁺ (1) with 3D diagrams (1) The candidate clearly links features on the diagrams with a characteristic of the stereoisomerism involved (1) Max: 9 [20] 2. Oxidation because oxidation state of Hg changes from 0 to +2 so oxidation (1) Reduction because oxidation number of O changes from -1 to -2 (1) Or Correct identification of all the oxidation numbers (1) Correct identification of oxidation and reduction (1) 2 Allow ecf for the identification of oxidation and reduction from wrong oxidation numbers

Plymstock School 1

[2]

[1]

4. (i)
$$(1s^22s^22p^6)3s^23p^63d^6$$
 (1)

1

1

(ii) Octahedral shape with some indication of three dimensions (1);

Bond angle 90° (1) *Allow* use of wedges and dotted lines to indicate three

2

Allow three dimensions if at least two bond angles of 900 are shown that clearly demonstrate 3D

If two different bond angles do not award bond angle mark

(iii) Green / olive green / dark-green / green-blue ppt (1)

Allow solid instead of precipitate

Allow solid or precipitate to be awarded from the state symbol in Fe(OH)₂(s)

$$Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_{2}(s)$$
 (1)

dimensions

[5]

5. (i)
$$MnO_2 + 4H^+ + 2Fe^{2+} \rightarrow Mn^{2+} + 2H_2O + 2Fe^{3+}$$
 (1)
Ignore state symbols

2

1

(ii) Moles of Fe²⁺ that reacted with $MnO_2 = 0.02 - 0.0123 = 0.0077$ (1) Allow ecf within question

Mass of MnO₂ =
$$0.00385 \times 86.9 = 0.335$$
 (1) % purity = 66.4% (1)
Allow $66.4 - 66.5$

Alternatively

Moles of MnO_2 in 0.504 = 0.00580

So moles of Fe^{2+} that should react with this is 0.0116 (1)

Moles of Fe^{2+} that reacted with $MnO_2 = 0.02 - 0.0123 = 0.0077$ (1) % purity = 66.4% (1)

[4]

3

1

6. (a) (i)
$$+3$$

		(ii)	Cis and trans forms drawn in 3-D (only award these marks if C has been chosen)	2	
		(iii)	Type of isomerism is cis-trans/geometric	1	
	(b)	(i) (ii)	(concentrated) hydrochloric acid/sodium chloride/ Other suitable named ionic chloride but <u>not</u> just chloride or Cl ⁻ Ligand substitution / ligand exchange	1	[6]
7.	(i)	Allov	blorised / add starch which is decolorised w blue/black → white or brown → white ot allow colourless	1	
	(ii)	Cu ²⁺ But 2	s $S_2O_3^{2-} = 23.20 \times 0.100/1000 = 0.00232$ moles $\equiv S_2O_3^{2-} / \text{ moles } \text{Cu}^{2+} = 0.00232$ moles 25 cm ³ of original = $10 \times 0.00232 = 0.0232$ moles centration of original = $1000 \times 0.0232 / 25$	1 1 1 1	
	(iii)		use concentration of Cu^{2+} is less than 1 mol dm ⁻³ / less than standard ibrium moves to left (reducing +ve value of E)	1 1	[7]
8.	(i)	$1s^22s$	$s^2 2p^6 3s^2 3p^6 3d^5$ (1)	1	
	(ii)		an incomplete set of d electrons / partially d sub-shell / partially filled d orbital (1) Allow partially filled d shell	1	[2]
9.	(i)		a (lone) pair of electrons that can be donated / lone pair that can form ive bond / pair of electrons that can form a coordinate bond (1)	1	

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3D diagram of octahedral structure (1);
      (ii)
                                                                                                     2
             Bond angle 90° (1)
                           Name
                           octahedral must be present to score two marks
                           Allow use of wedges and dotted lines to indicate three
                           dimensions
                           Allow three dimensions if at least two bond angles of 90° are
                           shown that clearly demonstrate 3D
                           If two different bond angles do not award bond angle mark
                                                                                                                 [3]
10.
      (i)
             Brown / red-brown / foxy-red / rusty / orange ppt (1)
                                                                                                     1
                           Allow solid instead of precipitate
                           Allow state symbol (s) for precipitate
             Fe^{3+}(aq) + 3OH^{-}(aq) \rightarrow Fe(OH)_{3}(s)
      (ii)
             Correct equation (1)
             State symbols for the correct formulae even if
             spectator ions are present (1)
                                                                                                     2
                           Allow equations using the hydrated iron(III) ion
                                                                                                                 [3]
     Fe_2O_3 + 3Cl_2 + 10OH^- \rightarrow 2FeO_4^{2-} + 5H_2O + 6Cl^- (2)
                                                                                                     2
                           Allow one mark if electrons shown
                           Allow one mark if correct reactants and products but not
                           balanced
                                                                                                                 [2]
12.
      Correct M<sub>r</sub> for Fe<sub>2</sub>O<sub>3</sub>, 159.6, and of Na<sub>2</sub>FeO<sub>4</sub>,165.8 (1)
       Moles of Fe_2O_3 = 0.00627 (1);
       Mass of Na_2FeO_4 = 2.08 (1);
      Percentage = 21.6 or 21.7 (%) (1)
                                                                                                     4
                           Allow full marks for correct answer with some working
                           Answer must have 3 sig figs
                           Allow ecf from wrong moles or wrong mass
                                                                                                                 [4]
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13.	Oxidation state of iron changes from +6 to +3 so is reduction (1)					
	Oxidation state of oxygen changes from -2 to 0 so is oxidation (1) To get the two marks for oxidation states marks any other oxidation state quoted must be correct. Maximum one mark if any other oxidation number given is wrong					
	OR					
	Oxidation state of iron changes from $+6$ to $+3$ and oxidation state of oxygen changes from -2 to 0 (1)					
	Iron is reduced and oxygen is oxidised (1) Allow ecf from wrong oxidation states	2	[2]			
14.	(i) (Oxidised to) iodine so a brown (solution) formed / Fe ³⁺ formed which is yellow or orange / Fe ²⁺ formed which is green (1) **Allow red/brown or orange**	1				
	(ii) Nitrogen / N_2 (1) Allow any correctly named oxide of nitrogen / correct formulae / HNO_3 etc.	1	[2]			
15.	$20 \text{ cm}^3 \text{ of } 0.100 \text{ mol dm}^{-3} \text{ VO}^{2+} = 0.002 \text{ moles}$ $0.002 \text{ moles VO}^{2+} = 0.0004 \text{ moles MnO}_4^-$ $0.0004 \text{ moles MnO}_4^- \text{ are in } 16.0 \text{ cm}^3$	1 1 1	[3]			
16.	(a) Ligand able to donate two lone pairs to form dative covalent / co-ordinate bonds	1 1				

3-D diagram with three ethanedioate ligands used

1 correct bonding between ligands and Cr³⁺

1 correct charge on ion (3–)

1 (Accept O — O as minimum for ethanedioate ion)

[5]

1

2

1

[8]

17. stereoisomers have same <u>structural</u> formula but a <u>different arrangement in space</u>

 $\begin{bmatrix} H_2O \\ H_2O \\ O \end{bmatrix} - \begin{bmatrix} H_2O \\ O \\ H_2O \end{bmatrix} - \begin{bmatrix} H_2O \\ H_2$

Diagrams of cis and trans isomers

$$\begin{bmatrix} H_2O & & \\ H_2O & & \\ & & \\ O & & \end{bmatrix} \begin{bmatrix} H_2O & \\ & & \\ O & & \\ & & \\ O & & \end{bmatrix}$$

Diagrams showing two optical isomers 2 (If diagrams are wrong / not used give 1 mark for mention of cis/trans and optical isomerism)

H₂O at 90°/ adjacent in cis / 180° / opposite in trans (not from diagram) 1
Optical isomers are non-superimposable mirror images 1

Quality of Written Communication:

At least three of the following key words used in context: non-superimposable, mirror images, optical, *cis/trans*, geometric, plane polarised, rotate, chiral, asymmetric

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Add (aqueous) sodium hydroxide which will give a brown/rusty ppt (1)
18.
                                                                                                  1
                          Allow solid for precipitate or (s) in equation
                          Allow Use aqueous thiocyanate ions which gives a (blood) red
                          colouration
                                                                                                              [1]
             Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}
19.
      (i)
             Correct reactants and products (1);
             Correct balancing (electrons cancelled out) (1)
                                                                                                  2
             Moles of dichromate(VI) = 3.53 \times 10^{-4} (1);
      (ii)
             Moles of iron(II) = 2.12 \times 10^{-3} (1):
             Moles of impure iron(II) sulphate = 2.36 \times 10^{-3} (1);
             Percentage purity = 89.8 / 89.8 - 90.0 (1)
                                                                                                  4
                          Allow alternative working out via mass instead of moles e.g.
                          mass of iron in hydrated FeSO4 from percentage composition
                          compared to mass of iron from moles of iron(II).
                          Allow ecf throughout unless percentage is above 100%
                                                                                                              [6]
20.
                    (Blue to) yellow (solution) / (blue to) green (solution) (1)
                                                                                                  1
      (a)
             (i)
             (ii)
                    Lone pair on chloride ion (1);
                    Donated to copper(II) ion (1)
                                                                                                  2
                          Allow dative bond / coordinate bond (1)
                          Allow marks via a diagram that must show lone pairs and the
                          dative bond
             (Light) blue precipitate / blue solid (1);
      (b)
             With excess (dark) blue solution (1)
                                                                                                  2
                          Not just goes blue
                                                                                                              [5]
21.
      Any three from
      Ammonia molecule 1 lone pair (and 3 bond pairs) (1);
      Ammonia ligand 4 bond pairs / lone pair is now a bond pair /
      ligand does not have a lone pair (1);
      Lone pairs repel more than bond pairs (1):
      In complex equal repulsion between electron pairs (1)
                                                                                                  3
                          Not bonds repel / atoms repel
                                                                                                              [3]
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- **22.** (i) 6
 - (ii) Species with (lone) pair of electrons
 Capable of being donated / forms a dative covalent
 bond / co-ordinate bond to a metal ion.
 (allow suitable diagram)
- [3]

23. (i) $[Co(H_2O)_6]^{2+}$ is octahedral $[CoCl_4]^{2-}$ is tetrahedral (both needed for 1 mark)

1

1

1

1

1

1

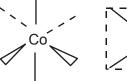
- (ii) pink to blue
- (iii) <u>Ligand</u> substitution / exchange/displacement

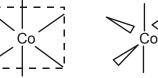
[3]

24. (a) (i) 1 mark for correct 3-D diagram of cis isomer 1 mark for correct 3-D diagram of trans isomer

(Allow planar diagrams if two appropriate 90° angles are shown)

Allow any suitable 3-D diagrams. Possibilities to include:



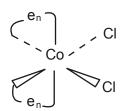


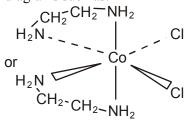
(ii) Geometric / cis – trans

- 1
- (b) 1 mark for using cis isomer 1 mark for correct 3-D diagrams which are mirror images of each other. 1

(If all diagrams are drawn as non-3d do not penalise in (b))

Allow any suitable 3-D diagrams such as:





[5]

25. (i) Brown solution/brown precipitate/black solid Add starch to get blue / black colour

1

(ii) Titration / volumetric analysis using sodium thiosulphate(with starch indicator)

1

(allow from equation)

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$
1 mol $Cr_2O_7^{2-} = 6 \text{ mols } S_2O_3^{2-}$
1
[5]

2

26. (a)
$$Zn^{2+}$$
 is $1s^22s^22p^63s^23p^63d^{10}$ and Cu^{2+} is $1s^22s^22p^63s^23p^63d^9$ (1);
Allow Zn^{2+} [Ar] $3d^{10}$ and Cu^2 [Ar] $3d^9$

Copper has at least one ion with an incomplete filled d-orbital (zinc does not) / copper(II) ion has an incomplete set of d electrons (zinc ion does not) / copper(II) ion has an incomplete d sub-shell (zinc ion does not) / ora (1)

(b) Cu²⁺ compounds are coloured but Zn²⁺ compounds are not (1);
Cu²⁺ compounds may be catalytic but Zn²⁺ compounds are not (1)

Allow Cu²⁺ forms complexes but Zn²⁺ does not

Allow correct chemistry of Cu²⁺ compared to Zn²⁺ e.g. Cu²⁺

and NaOH gives blue ppt but Zn²⁺ gives white ppt (that redissolves in excess)

[4]

27. Moles of hydrogen =
$$3.17 \times 10^{-3}$$
 / moles of zinc = 3.17×10^{-3} (1);
Not 3×10^{-3}

Mass of zinc = 0.207 g / moles of zinc \times 65.4 (1); **Not** 0.2

Not 0.2

Percentage of copper = 83.2 (1)

Allow ecf

Final answer must be to 3 or 4 sig figs

Penalise significant figures just once

Allow values between 82.9–83.2

28. (i)
$$Cu \rightarrow Cu^{2+} + 2e^{-}/Cu - 2e^{-} \rightarrow Cu^{2+}$$
 (1) 1
(ii) $2Cu + O_2 + 4H^+ \rightarrow 2Cu^{2+} + 2H_2O$ (1) 1
Allow any correct multiple
Allow ecf from (a)(i)

[2]

29.
$$M_{\rm r}$$
 of $[{\rm Cu}({\rm CH_3COO})_2]_2.{\rm Cu}({\rm OH})_2 = 460.5$ (1) *Allow ecf from wrong* $M_{\rm r}$

Molar ratio
$$[Cu(CH_3COO)_2]_2$$
. $Cu(OH)_2$: H_2O is 0.182: 0.906 (1) $x = 5$ (1)

Not full marks for 5 with no working out

[3]

30. Ligand substitution

Suitable example e.g. reaction of thiocyanate ions with hexaaquairon(III) to give $[Fe(H_2O)_5(CNS)]^{2+}$ (1);

Observations *e.g.* formation of a blood-red colour (1) Suitable equation e.g.

$$[Fe(H_2O)_6]^{3+} + CNS^- \rightarrow [Fe(H_2O)_5(CNS)]^{2+} + H_2O$$
 (1)

Suitable example can be awarded from an equation Equations do not need state symbols

Precipitation

Suitable example e.g. reaction between (aqueous) iron(II) chloride with (aqueous) sodium hydroxide (1);

Observations e.g. formation of a green precipitate / formation of a green solid (1)

Suitable equation e.g. $Fe^{2+}(aq) + 2OH(aq) \rightarrow Fe(OH)_2(s)$ (1)

Precipitate can be awarded state symbol in equation

Redox

Suitable example e.g. oxidation of iron(II) chloride by chlorine to make iron(III) chloride (1)

Observation e.g. green solution becomes yellow / rust solution (1)

Suitable equation e.g. $2\text{FeC}l_2 + \text{C}l_2 \rightarrow 2\text{FeC}l_3$ (1)

Other examples could include iron and chlorine to make iron(III) chloride / iron and HCl to make $FeCl_2/MnO_4^-$ and Fe^{2+} to make Fe^{3+}

And QWC

One mark for correct spelling, punctuation and grammar in at least two sentences (1) 10

Answer must address the question

[10]

1

1

- 31. (a) $1s^22s^22p^63s^23p^63d^8$ (Do not accept [Ar]3d⁸)
 - (b) (i) Ring around O⁻ 1 Ring around N 1

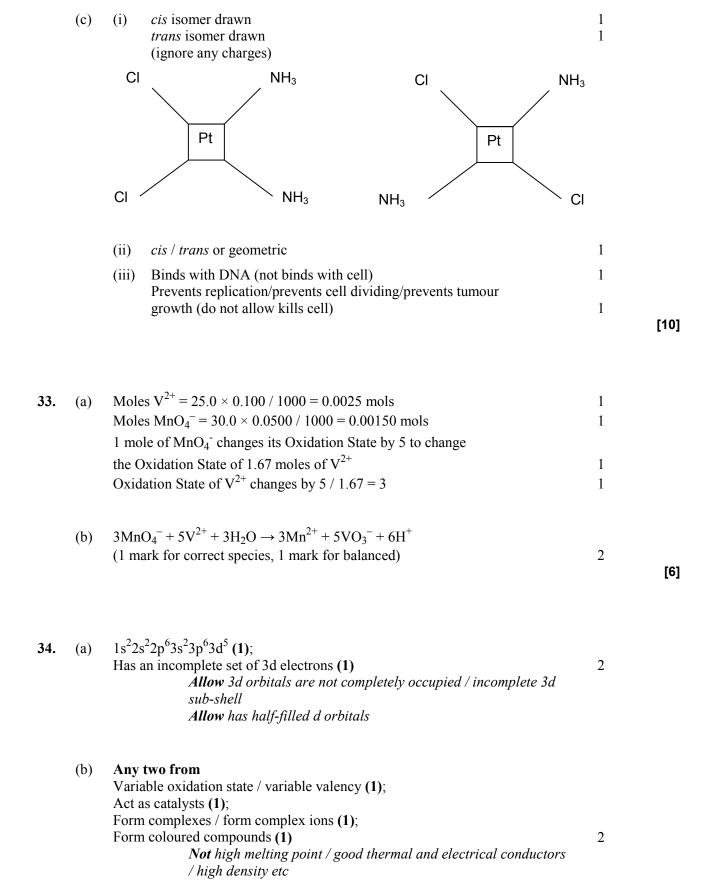
(ii) <u>Lone pair (of electrons) / non-bonding pair</u> 1

[4]

32. (a) (i) Number of dative bonds / co-ordinate bonds formed with the transition metal (Do not accept number of ligands but allow number of lone pairs bonded to....)

(Accept ring around O of C=O as an alternative to O⁻)

- (ii) Square planar 1
- (b) (i) Ligand substitution 1
 - (ii) x = -2 1 1 1



	(c)	Iron (II) ions give a green ppt (1); Iron (III) ions give an orange-rust ppt (1) Precipitate must be used once Allow solid instead of ppt	2	
	(d)	$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$ Correct reactants and products (1); Correct balancing (1)	2	[8]
35.	(i)	Copper may react with potassium manganate(VII) / iron(III) ions formed in titration may be reduced back to iron(II) ions by the copper (1)	1	
	(ii)	$\mathrm{MnO_4}^-$ gains electrons and is reduced / Mn oxidation state changes from +7 to +2 so it is reduced (1); Fe ²⁺ loses electrons and is oxidised / Fe oxidation state changes from +2 to +3 so it is oxidised (1)	2	
	(iii)	Moles of $MnO_4^- = 4.50 \times 10^{-4}$ (1); Moles of $Fe^{2+} = 5 \times moles \ MnO_4^- / 2.25 \times 10^{-3}$ (1); Mass of $Fe = moles \ of \ Fe^{2+} \times 55.8 / 0.1256$ (1); Percentage = 18.6 % (1) Allow answers that use 56 for A_r of Fe this gives 18.7 Allow ecf	4	[7]
36.	(a)	(Pale blue solution) to a (light) blue ppt (1); with excess dark blue solution (1)	2	
	(b)	Octahedral shape with clear indication of 3D either by construction lines or wedges etc (1); 90° (1) Ignore mistakes with the ligands question focuses on octahedral and the bond angle	2	[4]

Water molecule 2 lone pairs (and 2 bond pairs) (1); 37. Water ligand 1 lone pair and 3 bond pairs / lone pair is now a bond pair / water has one less lone pair when it is a ligand (1); 3 Lone pairs repel more than bond pairs (1) Not atoms repel [3] 38. (i) Central ion surrounded by molecules/ions/ligands 1 Molecule/ion with a lone pair of electrons (ii) 1 Able to form a dative covalent or co-ordinate bond / which can be donated 1 [3] 39. Two lone pairs/ able to form two dative covalent / co-ordinate bonds 1 (a) Stereoisomerism – same atoms with same order of bonds but a (b) different spatial arrangement / same structure but different arrangement of atoms 1 Both isomers drawn for cis / trans 2 Both isomers drawn for optical (must be mirror images) 2 (all diagrams to show 3-D arrangement) Enantiomers/non superimposable mirror images 1 Rotate plane polarised light in opposite direction by same number of degrees (any two for 1 mark) 1 [8] $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightleftharpoons 2Cr^{3+} + 3I_2 + 7H_2O$ 40. (i) All species correct (ignore electrons for this mark) 1 Equation balanced (penalise if electrons not cancelled out) 1 (ii) Brown colour disappears 1 $S_2O_3^{2-}$ reacts with I_2 (to form colourless I^-) 1 Green colour remains due to Cr³⁺ (must say what gives green colour) 1 [5]

41. Transition element

 $Cu^{2+} 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$ (1);

Transition elements have one oxidation state that has an

incomplete set of 3d electrons / have one ion with a half-filled 3d orbital (1)

Allow has at least one half-filled d orbital / partially filled 3d sub-shell

Complex ion

Example of a **copper** complex ion e.g. $[Cu(H_2O)_6]^{2+}$ or $CuCl_4^{2-}$ (1);

Diagram of the copper complex showing three

dimensions e.g. use of wedges or dotted lines (1);

Correct bond angle to match the complex / correct name

of the shape of the complex (1);

If a copper complex that does not exist is used then first three marks not available

If a correct iron complex is given then example mark cannot be awarded

Allow square planar where appropriate

Ligand is an electron pair donor (1);

Copper(II) ion is an electron pair acceptor (1);

Dative bond exists between ligand and the copper(II) ion (1)

Electron pair donor, electron pair acceptor and dative bond marks can awarded from an appropriate diagram

Properties

Several oxidation states e.g. copper has +1 and +2 or iron has +2 and +3 (1);

Ignore copper has a +3

Ignore iron has a +6 *oxidation state*

Forms coloured compounds e.g. copper(ii) chloride is

green or iron(II) sulphate is pale green (1);

Element or compound has catalytic properties

e.g. Iron is a catalyst in the Haber process (1)

11

Quality of written communication

Use of technical terms – at least three terms from the following list are used in the correct context

- ligand
- dative bond
- coordinate bond
- tetrahedral
- square planar
- octahedral
- oxidation (state)
- catalyst
- electron pair
- lone pair
- orbital
- sub-shell (1)

Put a ring around the technical terms

1

[12]

- 42. 1 (a) (i) Zinc
 - (ii) Coins + resist corrosion (not rusting) / hard wearing Or statues + resist corrosion/ attractive patina Or electrical connections + good conductor Or musical instruments + attractive / sonorous Or plumbing fixtures + hard / corrosion resistant 1
 - (b) (i) Sodium carbonate/sodium hydroxide/other suitable named alkali (accept correct formulae) 1 Do not accept 'alkali' on its own
 - (ii) Starch 1
 - Just before the end point/when solution turns pale straw 1 (iii)
 - (c) (i) 0.002 mol 1

		(ii)	One (1)	1	
		(iii)	0.002 mol	1	
		(iv)	0.002 mols Cu^{2+} contains 0.002×63.5 g of $Cu = 0.127$ g 250 cm ³ of solution contains 10×0.127 g = 1.27 g % $Cu = 1.27/1.65 \times 100 = 77.0\%$ (Allow 76.9-77.0; allow ecf)	1 1 1	
			(Tillow 70.5 77.0, allow cell)		[11]
43.	(a)		aber of coordinate / dative covalent bonds attached etal ion / number of lone pairs accepted (not number of ligands)	1	
	(b)	(i)	$[\text{Co}(\text{H}_2\text{O})_6]^{2^+}$ is octahedral; $[\text{CoC}l_4]^{2^-}$ is tetrahedral Drawings must be 3 dimensional		
			Acceptable shapes for $[Co(H_2O)_6]^{2+}$ include:		
		1			
			Acceptable shapes for $[CoCl_4]^{2-}$ include Co Co.		
				2	
		(ii)	$Pink \rightarrow blue$	2	
		(iii)	Add water. (Allow other suitable suggestions, e.g. add lead nitrate to		

1

1

1

[6]

[3]

precipitate $C\Gamma$ as $PbCl_2$)

Prevents cell from replicating / cells die

(i)

(ii)

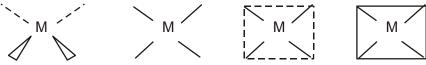
44.

Cis platin

Binds to DNA

45.	(Cis/trans) + Examples (must be 3-d drawings)	2	
	Correctly labelled as cis and trans (allow this mark if diagrams are planar)	1	
	Cis has same atoms at 90° + Trans has same atoms at		
	180° (need reference to bond angles for mark)	1	
	(Optical) + examples (must be 3-d drawings)	2	
	Rotate plane polarised light (by same number of		
	degrees) in opposite directions	1	
	Non-superimposable mirror images	1	
	NB If use H ₃ N CH ₂ CH ₂ NH ₃ penalise only once		

Any example which show the principle of cis/trans isomerism and optical isomerism are fine but, all diagrams must be 3-d. The shapes shown in the previous question are allowed for octahedral or tetrahedral. For square planar complexes used to illustrate cis/trans isomerism the following illustrations are fine. For optical isomerism, there must be a mirror line and the isomers must be non-superimposable object/mirror images.



QWC – to be awarded for the correct use of scientific terms, to include at least 3 of the following: Cis & trans, optical, plane, polarised, non-superimposable, mirror images, geometric, bidentate, ligand, octahedral, square planar, tetrahedral

[9]

1