Marks
2

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of Co^{2+}.

Co^{2+} has a 3*d*^{7} configuration:

↑↓	↑↓	↑	↑	↑

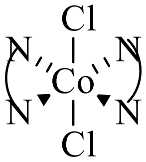
Co^{2+} is a *d*^{7} system, so must have at least 1 unpaired electron. Consequently it must be paramagnetic.

Marks
4

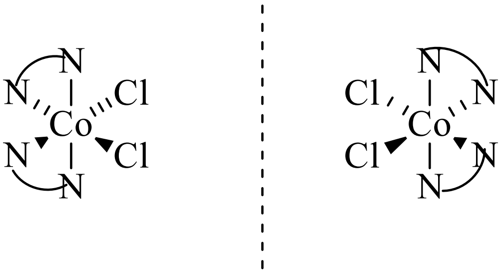
- Name the complex $[CoCl_2(en)_2]$. en = ethylenediamine = $NH_2CH_2CH_2NH_2$

dichloridobis(ethylenediamine)cobalt(II)

Draw all possible isomers of this complex.



trans isomer



cis isomers

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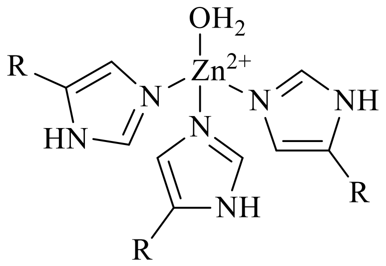
Marks
7

- The structure below represents the active site in carbonic anhydrase, which features a Zn^{2+} ion bonded to 3 histidine residues and a water molecule.



The pK_a of uncoordinated water is 15.7, but the pK_a of the water ligand in carbonic anhydrase is around 7. Suggest an explanation for this large change.

The high charge on the Zn^{2+} ion draws electron density out of the O–H bonds in the water molecule. This weakens the O–H so the H^+ is more likely to leave.

The water in carbonic anhydrase is therefore more acidic, as shown by the large decrease in pK_a.

When studying zinc-containing metalloenzymes, chemists often replace Zn^{2+} with Co^{2+}. Using the box notation to represent atomic orbitals, work out how many unpaired electrons are present in the Zn^{2+} and Co^{2+} ions.

Zn^{2+}, $3d^{10}$	↑↓	↑↓	↑↓	↑↓	↑↓
Co^{2+}, $3d^{7}$	↑↓	↑↓	↑	↑	↑

Zn^{2+} has 0 unpaired *d* electrons, Co^{2+} has 3 unpaired *d* electrons. Co^{2+} is therefore paramagnetic and will be attracted by a magnetic field.

Suggest why it is useful to replace Zn^{2+} with Co^{2+} when studying the nature of the active site in carbonic anhydrase.

The ions have similar radii so the properties of natural carbonic anhydrase and the version with cobalt replacing zinc should have similar biological properties. The unpaired electrons on Co^{2+} however mean that it is paramagnetic and the magnetism can be used to study the active site.

Suggest two differences in the chemistry of Zn^{2+} and Co^{2+} ions that may affect the reactivity of the cobalt-containing enzyme.

Zinc only forms +2 ions but cobalt forms +2 and +3. The cobalt-containing enzyme may be susceptible to oxidation.

Zn^{2+} tends to form 4-coordinate tetrahedral complexes but Co^{2+} is slightly larger and often forms 6-coordinate octahedral complexes. The metal ion may change its coordination by bonding extra ligands.

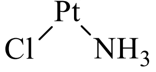
Marks
8

- Use the information already provided to complete the following table.
  (ox = oxalate = $C_2O_4^{2-}$)

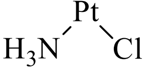
Formula	$[CrCl_2(NH_3)_4]^n$	$[Fe(ox)_3]^n$	$[ZnCl_2(NH_3)_2]^n$
Oxidation state of transition metal ion	**+III**	+III	**+II**
Number of *d*-electrons in the transition metal ion	**3**	**5**	10
Number of unpaired *d*-electrons in the transition metal ion	**3**	**5**	**0**
Charge of complex (*i.e.* n)	1+	**3-**	**0**
Is the metal atom paramagnetic?	**Yes**	**Yes**	**No**

The complex $[PtCl_2(NH_3)_2]$ has two isomers, while its zinc analogue (in the table) exists in only one form. Using diagrams where appropriate, explain why this is so.

The Pt compound has square planar geometry and hence 2 isomers, where the Cl groups are either opposite each other (*trans*) or next to each other (*cis*). The Zn compound has tetrahedral geometry and hence only one structure exists



cis-isomer



trans-isomer

Marks
6

- Complete the following table.

Formula	Geometry of complex	Ligand donor atom(s)
$[Zn(OH)_4]^{2-}$	**tetrahedral**	**O**
$[CoCl(NH_3)_5]SO_4$	**octahedral**	**Cl and N**
$K_4[Fe(CN)_6]$	**octahedral**	**C**
$[Ag(CN)_2]^-$	**linear**	**C**

Select any complex ion from the above table and state whether it is paramagnetic, diamagnetic or neither. Explain your reasoning.

Zn^{2+} is d^{10} system. No unpaired electrons, therefore diamagnetic.

↑↓	↑↓	↑↓	↑↓	↑↓

Co^{3+} is d^6 system. 2 paired electrons and 4 unpaired, therefore paramagnetic.

↑↓	↑	↑	↑	↑

Fe^{2+} is d^6 system. 2 paired electrons and 4 unpaired, therefore paramagnetic.

↑↓	↑	↑	↑	↑

Ag^+ is d^{10} system. No unpaired electrons, therefore diamagnetic.

↑↓	↑↓	↑↓	↑↓	↑↓

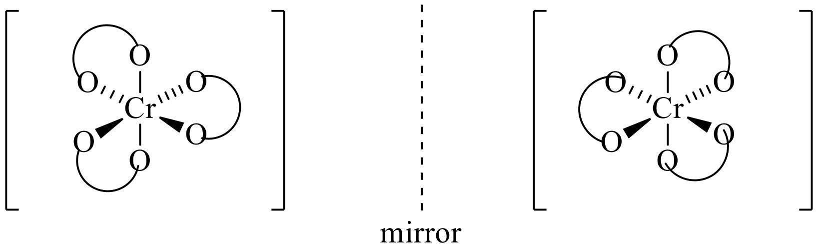
Marks
3

- Which of the following complexes is/are chiral? Explain your reasoning. Use diagrams where necessary.

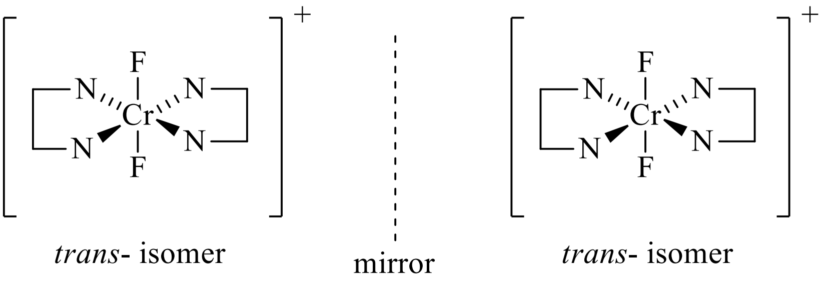
acetylacetonate ion = $CH_3COCHCOCH_3^-$

ethylenediamine = $NH_2CH_2CH_2NH_2$

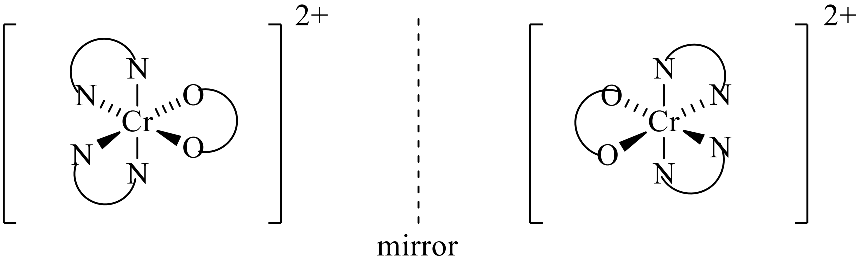
tris(acetylacetonato)chromium(III) is chiral – mirror images are non-superimposable



***trans*-bis(ethylenediamine)difluoridochromium(III) ion is not chiral – it is identical to its mirror image.**



acetylacetonatobis(ethylenediamine)chromium(III) ion is chiral – mirror images are non-superimposable



Marks
7

- What is the solubility of $Cu(OH)_2$ in mol L^{-1}? K_{sp} ($Cu(OH)_2$) is 1.6×10^{-19} at 25 °C.

The dissolution reaction and associated solubility product are:

$$\mathbf{Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq) \qquad K_{sp} = [Cu^{2+}(aq)][OH^-(aq)]^2}$$

If x mol dissolve in one litre, $[Cu^{2+}(aq)] = x$ M and $[OH^-(aq)] = 2x$. Hence:

$$\mathbf{K_{sp} = (x)(2x)^2 = 4x^3 = 1.6 \times 10^{-19}}$$

$$\mathbf{x = 3.4 \times 10^{-7}\ M}$$

Answer: **3.4×10^{-7} M**

The overall formation constant for $[Cu(NH_3)_4]^{2+}$ is 1.0×10^{13}. Write the equation for the reaction of Cu^{2+} ions with excess ammonia solution.

$$\mathbf{Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)}$$

Calculate the value of the equilibrium constant for the following reaction.

$$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$$

This reaction can be considered to occur via (i) $Cu(OH)_2$ dissolving followed by (ii) the $Cu^{2+}(aq)$ ions that form being complexed by ammonia.

For the formation of $[Cu(NH_3)_4]^{2+}$, the equilibrium constant is:

$$\mathbf{K_{stab} = \frac{[Cu(NH_3)_4{}^{2+}]}{[Cu^{2+}][NH_3]^4} = 1.0 \times 10^{13}}$$

For the reaction of $Cu(OH)_2(s)$ with $NH_3(aq)$, the equilibrium constant is:

$$\mathbf{K = \frac{[Cu(NH_3)_4{}^{2+}][OH^-(aq)]^2}{[NH_3]^4}}$$

To obtain K, K_{sp} is multiplied by K_{stab}:

$$\mathbf{K = K_{sp} \times K_{stab}}$$

$$\mathbf{= \cancel{[Cu^{2+}(aq)]}[OH^-(aq)]^2 \times \frac{[Cu(NH_3)_4{}^{2+}]}{\cancel{[Cu^{2+}]}[NH_3]^4} = \frac{[Cu(NH_3)_4{}^{2+}][OH^-(aq)]^2}{[NH_3]^4}}$$

$$\mathbf{= (1.6 \times 10^{-19}) \times (1.0 \times 10^{13}) = 1.6 \times 10^{-6}}$$

Answer: **1.6×10^{-6}**

Would you expect $Cu(OH)_2(s)$ to dissolve in 1 M NH_3 solution? Briefly explain your answer.

No. Equilibrium constant *K* is very small so the reaction lies heavily in favour of reactants.

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of Cu^{2+}.

2

Cu^{2+} is d^9

↑↓	↑↓	↑↓	↑↓	↑

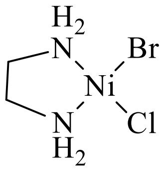
is paramagnetic

- Provide a systematic name for the complex [NiBrCl(en)] and draw both of its possible structures. (en = $NH_2CH_2CH_2NH_2$ = ethylenediamine = ethane-1,2-diamine)

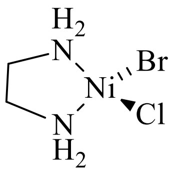
4

Both of the following names are acceptable:

- **bromidochlorido(ethylenediamine)nickel(II)**
- **bromidochlorido(ethane-1,2-diamine)nickel(II)**



square planar



tetrahedral

Is either complex chiral? Explain your reasoning.

No. Both structures are superimposable on (*i.e.* identical to) their mirror images.

- Complete the following table. (ox = oxalate = $C_2O_4^{2-}$)

Marks
6

Formula	$Na[FeCl_4]$	$[CrCN(NH_3)_5]Br_2$	$K_3[VO_2(ox)_2]\cdot 3H_2O$
Oxidation state of transition metal ion	**+III**	**+III**	**+V**
Coordination number of transition metal ion	**4**	**6**	**6**
Number of *d*-electrons in the transition metal ion	**5**	**3**	**0**
Species formed upon dissolving in water	**$Na^+(aq)$, $[FeCl_4]^-(aq)$**	**$[CrCN(NH_3)_5]^{2+}(aq)$, $Br^-(aq)$**	**$K^+(aq)$, $[VO_2(ox)_2]^{3-}(aq)$**

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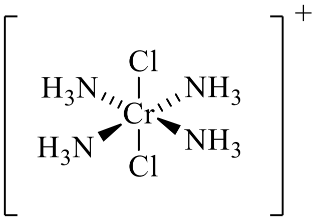
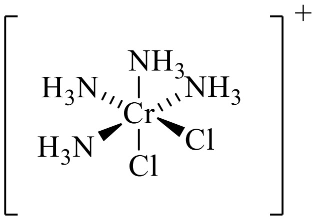
Marks
9

- The following three complex ions can all exhibit isomerism. Name the type of isomerism involved in each case and draw the structures of the isomeric pairs.
  ox = oxalate = $C_2O_4^{2-}$

$[CrCl_2(NH_3)_4]^+$



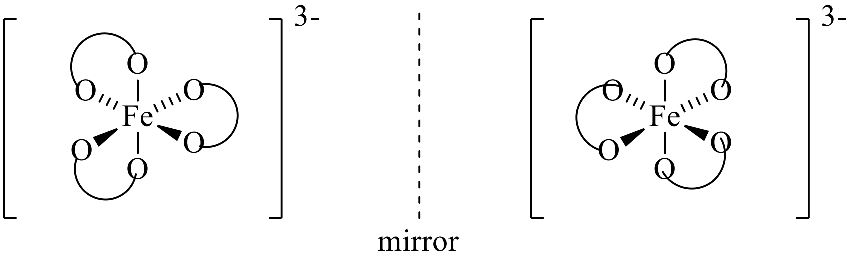
trans- isomer



cis- isomer

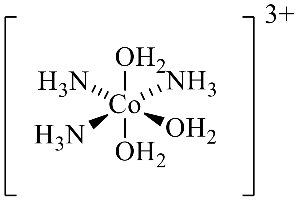
Geometrical isomerism

$[Fe(ox)_3]^{3-}$



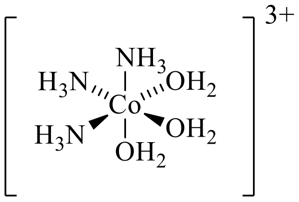
Optical isomerism

$[Co(NH_3)_3(OH_2)_3]^{3+}$



mer- isomer

the OH_2 ligands lie along a meridian



fac- isomer

the OH_2 ligands define a face of an octahedron

Geometrical isomerism

3

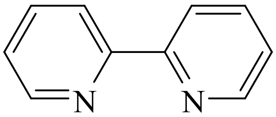
- Give the systematic name of each of the following compounds.
  en = ethylenediamine = 1,2-diaminoethane = $NH_2CH_2CH_2NH_2$

$Cs_2[PtF_6]$	**caesium hexafluoridoplatinate(IV)**
$[Co(en)_2(NH_3)_2]Br_3$	**diamminebis(ethylenediamine)cobalt(III) bromide**

Marks
5

- Complete the following table. NCS^- = isothiocyanate ion

bipy = 2,2'-bipyridine = $(C_5H_4N)_2$ =



Formula	$K_2[Zn(CN)_4]$	$[Co(bipy)(NH_3)_4]Cl_3$	$[Co(bipy)_2(NCS)_2]$
Oxidation state of transition metal ion	**+2 or II**	**+3 or III**	**+2 or II**
Coordination number of transition metal ion	**4**	**6**	**6**
Number of *d*-electrons in the transition metal ion	**10**	**6**	**7**
Coordination geometry of the complex ion	**tetrahedral**	**octahedral**	**octahedral**
List all the ligand donor atoms	**4 × C**	**2 × N (from bipy)** **4 × N (from NH_3)**	**4 × N (from bipy)** **2 × N (from NCS^-)**

- Titanium has three common oxidation states, +II, +III and +IV. Using the box notation to represent atomic orbitals, predict whether compounds of Ti^{2+}, Ti^{3+} and Ti^{4+} would be paramagnetic or diamagnetic. 2

Ti is in group 4: it has 4 valence electrons. Ti^{2+} therefore has (4 – 2) = 2 remaining: it has a d^2 configuration. Ti^{3+} therefore has (4 – 3) = 1 remaining: it has a d^1 configuration. Ti^{4+} therefore has (4 – 4) = 0 remaining: it has a d^0 configuration.

These electrons are arranged in the five *d* orbitals to minimise the repulsion between them. This is achieved by keeping the maximum number possible unpaired.

Ti^{2+}	↑	↑			
Ti^{3+}	↑				
Ti^{4+}					

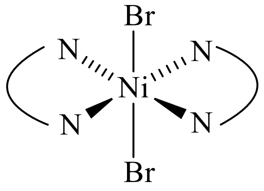
Ti^{2+} and Ti^{3+} have unpaired electrons and are paramagnetic. Ti^{4+} has no unpaired electrons and is diamagnetic.

- Provide a systematic name for the complex *trans*-$[NiBr_2(en)_2]$ and draw its structure. Is this complex chiral? Explain your reasoning. 4

  en = ethylenediamine = ethane-1,2-diamine

***trans*-dibromidobis(ethylenediamine)nickel(II) or**
***trans*-dibromidobis(ethane-1,2-diamine)nickel(II)**

It is not chiral as it is superimposable on (*i.e.* identical to) its mirror image.



Marks
5

- Complete the following table. (EDTA = ethylenediaminetetraacetate)

Formula	$[Ni(NH_3)_6](NO_3)_2$	*trans*-$[PtCl_2(NH_3)_2]$	$Na[Fe(EDTA)]$
Oxidation state of transition metal ion	**+II**	**+II**	**+III**
Coordination number of transition metal ion	**6**	**4**	**6**
Number of *d*-electrons in the transition metal ion	**8**	**8**	**5**
Coordination geometry of the complex ion	**octahedral**	**square planar**	**octahedral**
List all the ligand donor atoms	**N**	**Cl, N**	**N, O**

Marks
2

- Explain in terms of their electronic configurations **and** ionisation energies why the halogens (Group 17) are powerful *oxidising* agents.

Oxidising agents are themselves reduced (*i.e.* they gain electrons).

The electronic configuration of the halogens (Group 17) is np^5. They are small atoms (atomic size decreases across a period as the nuclear charge increases). In each period, the halogen is the element with the highest number of protons in the nucleus that also has an incomplete shell.

As a result, they will readily gain a single electron to form the X^- ion.

Similarly, the high nuclear charge and small size means that they have high ionisation energies. Hence halogens are poor reducing agents.

Marks
9

- Complete the following table. (en = ethylenediamine = $NH_2CH_2CH_2NH_2$)

Formula	$K_2[CoCl_4]$	$Na_3[FeBr(CN)_5]$	$[Zn(en)_2(NO_3)_2]$
Oxidation state of transition metal ion	**+2 (II)**	**+3 (III)**	**+2 (II)**
Coordination number of transition metal ion	**4**	**6**	**6** **(4 × N from en and 2 × O from NO_3^-)**
Number of *d*-electrons in the transition metal ion	**7** **(Co is in Group 9 so Co^{2+} has 9 – 2= 7)**	**5** **(Fe is in Group 8 so Fe^{3+} has 8 – 3 = 5)**	**10** **(Zn is in Group 12 Zn^{2+} has 12 – 2= 10)**
Charge of the complex ion	**2–** **$[CoCl_4]^{2-}$**	**3–** **$[FeBr(CN)_5]^{3-}$**	**0** **$[Zn(en)_2(NO_3)_2]$**
Geometry of the complex ion	**tetrahedral**	**octahedral**	**octahedral**
List all the ligand donor atoms	**4 × Cl**	**1 × Br and 5 × C**	**4 × N and 2 × O**

- Explain why compounds of *d*-block elements are frequently paramagnetic. Use examples in your answer. **2**

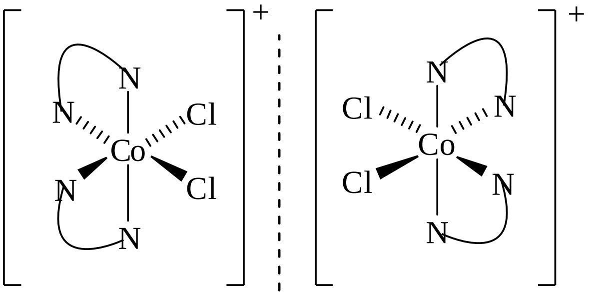
Paramagnetism is the property of a compound to be attracted by an external magnetic field. It is a characteristic of any compound with unpaired electrons. *d*-Block elements have from 1 to 10 electrons in the *d*-orbitals. When forming compounds, some of these may be lost to give paramagnetic species. Species with odd numbers of electrons must be paramagnetic, species with even numbers of *d*-electrons, may or may not be paramagnetic. eg

Cu^{2+}, d^9	↑↓	↑↓	↑↓	↑↓	↑	**must be paramagnetic**
Zn^{2+}, d^{10}	↑↓	↑↓	↑↓	↑↓	↑↓	**must be diamagnetic**
Fe^{2+}, d^6	↑↓	↑	↑	↑	↑	**is paramagnetic**

- Provide a systematic name for *cis*-$[Co(en)_2Cl_2]Cl$. Is this complex chiral? Explain your reasoning by drawing the structure of the complex. **3**
  en = $NH_2CH_2CH_2NH_2$ = ethane-1,2-diamine = ethylenediamine

***cis*-dichloridobis(ethylenediamine)cobalt(III) chloride or**
***cis*-dichloridobis(ethane-1,2-diamine)cobalt(III) chloride**

The complex is chiral as it is not superimposable on its mirror image.



3

- Derive expressions for the equilibrium constants for the complexation of Pb^{2+} (K_1) and of Ca^{2+} (K_2) by $EDTA^{4-}$.

$$\mathbf{Pb^{2+} + EDTA^{4-} \rightleftharpoons [Pb(EDTA)]^{2-}} \quad K_1 = \frac{[\mathrm{Pb(EDTA)}^{2-}]}{[\mathrm{Pb}^{2+}][\mathrm{EDTA}^{4-}]}$$

$$\mathbf{Ca^{2+} + EDTA^{4-} \rightleftharpoons [Ca(EDTA)]^{2-}} \quad K_2 = \frac{[\mathrm{Ca(EDTA)}^{2-}]}{[\mathrm{Ca}^{2+}][\mathrm{EDTA}^{4-}]}$$

Briefly explain why the chelating agent, EDTA, is administered as $[Ca(EDTA)]^{2-}$ to treat lead poisoning and determine which of K_1 or K_2 must be greater for the therapy to be effective.

K_1 must be greater than K_2 for the therapy to be effective.

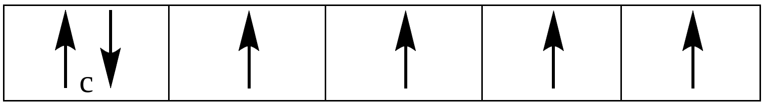
$[Ca^{2+}]$ is much greater than $[Pb^{2+}]$ in the body, so need $K_1 > K_2$ to form the Pb complex. If EDTA is not administered as the Ca complex, it will strip Ca^{2+} from the body.

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, explain why most Fe^{2+} and Fe^{3+} compounds are paramagnetic. **2**

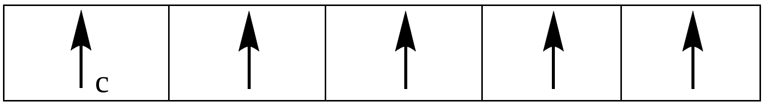
Iron is in Group 8 and thus has 8 valence electrons. Fe^{2+} thus has (8 – 2) = 6 electrons and Fe^{3+} has (8 – 3) = 5 electrons. These electrons occupy the 3*d* orbitals and do so to minimize the number of electron pairs, and thus minimize electron / electron repulsion.

There are five 3*d* orbitals and thus the configurations are:

Fe^{2+} $3d^6$



Fe^{3+} $3d^5$



With 4 and 5 unpaired electrons respectively, both Fe^{2+} and Fe^{3+} are paramagnetic.

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- Complete the following table. (en = ethylenediamine = $NH_2CH_2CH_2NH_2$)

Marks
9

Formula	$(NH_4)_2[CoCl_4]$	$[Cr(NH_3)_5(H_2O)]Cl_3$	*cis*-$[PtCl_2(en)_2]$
Oxidation state of transition metal ion	**+2 (II)**	**+3 (III)**	**+2 (II)**
Coordination number of transition metal ion	**4**	**6**	**6** **(2 × Cl and 4 × N from 2en)**
Number of *d*-electrons in the transition metal ion	**7** **(Co is in Group 9 so Co^{2+} has 9 – 2= 7)**	**3** **(Cr is in Group 6 so Co^{2+} has 6 – 3= 3)**	**8** **(Pt is in Group 10 so Pt^{2+} has 10 – 2= 8)**
Charge of the complex ion	**-2** **$[CoCl_4]^{2-}$**	**+3** **$[Cr(NH_3)_5(OH_2)]^{3+}$**	**0** **$[PtCl_2(en)]$**
Geometry of the complex ion	**tetrahedral**	**octahedral**	**octahedral**
List all the ligand donor atoms	**4 × Cl^-**	**5 × N and 1 × O**	**2 × Cl^- and 4 × N**

- Calculate the equilibrium constant for the following reaction.

$$\mathrm{AgI(s)} + 2\mathrm{CN^-(aq)} \rightleftharpoons [\mathrm{Ag(CN)_2}]^-\mathrm{(aq)} + \mathrm{I^-(aq)}$$

Data: K_{stab} of $[\mathrm{Ag(CN)_2}]^- = 3 \times 10^{20}$; K_{sp} of AgI = 8.3×10^{-17}

The equations for the dissolution of AgI and the stability constant of the complex $[\mathrm{Ag(CN)_2}]^-$ are, respectively:

$$\mathrm{AgI(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{I^-(aq)} \qquad K_{\mathrm{sp}} = [\mathrm{Ag^+(aq)}][\mathrm{I^-(aq)}]$$

$$\mathrm{Ag^+(aq)} + 2\mathrm{CN^-(aq)} \rightleftharpoons [\mathrm{Ag(CN)_2}]^-\mathrm{(aq)} \qquad K_{\mathrm{stab}} = \frac{[[\mathrm{Ag(CN)_2}]^-\mathrm{(aq)}]}{[\mathrm{Ag^+(aq)}][\mathrm{CN^-(aq)}]^2}$$

Addition of these reactions gives the required reaction and so the equilibrium constant for the reaction is the product of the individual equilibrium constants:

$$\mathrm{AgI(s)} + 2\mathrm{CN^-(aq)} \rightleftharpoons [\mathrm{Ag(CN)_2}]^-\mathrm{(aq)} + \mathrm{I^-(aq)}$$

$$K = K_{\mathrm{sp}} \times K_{\mathrm{stab}} = [\mathrm{Ag^+(aq)}][\mathrm{I^-(aq)}] \times \frac{[[\mathrm{Ag(CN)_2}]^-\mathrm{(aq)}]}{[\mathrm{Ag^+(aq)}][\mathrm{CN^-(aq)}]^2}$$

$$= \frac{[[\mathrm{Ag(CN)_2}]^-\mathrm{(aq)}][\mathrm{I^-(aq)}]}{[\mathrm{CN^-(aq)}]^2}$$

Hence,

$$K = K_{\mathrm{sp}} \times K_{\mathrm{stab}} = (8.3 \times 10^{-17}) \times (3 \times 10^{20}) = 2 \times 10^4$$

Answer: **2×10^4**

Marks
2

- Which of the cations, $[Fe(OH_2)_6]^{3+}$ and $[Fe(OH_2)_6]^{2+}$, has the larger pK_a? Briefly explain why.

Solutions containing both cations are acidic due to the equilibria:

$$[Fe(OH_2)_6]^{2+}(aq) \rightleftharpoons [Fe(OH_2)_5(OH)]^{+}(aq) + H^{+}(aq)$$
$$[Fe(OH_2)_6]^{3+}(aq) \rightleftharpoons [Fe(OH_2)_5(OH)]^{2+}(aq) + H^{+}(aq)$$

The Fe^{2+} and Fe^{3+} cations polarize the Fe-OH_2 bond, pulling electron density from the oxygen. The oxygen, in turn, pulls electron density away towards itself in the O-H bond, causing H^+ to be produced.

Fe^{3+} has a higher charge and is smaller than Fe^{2+}: it is more polarizing and so $[Fe(OH_2)_6]^{3+}$ is more acidic. The equilibrium is further to the right for $[Fe(OH_2)_6]^{3+}$ than it is for $[Fe(OH_2)_6]^{2+}$ so $K_a([Fe(OH_2)_6]^{3+}) > K_a([Fe(OH_2)_6]^{2+})$.

As p$K_a = -\log_{10}K_a$, a higher K_a means a *lower* pK_a. Thus, $[Fe(OH_2)_6]^{3+}$ is the more acidic of the two cations and has the lower pK_a value.

3

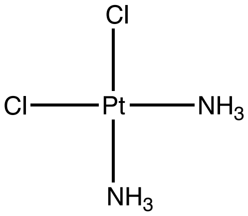
- Consider the compound $[CrCl(OH_2)_4(NCS)]Cl\cdot 2H_2O$.
The complex ion is $[CrCl(OH_2)_4(NCS)]^+$. This contains Cr^{3+} bonded to Cl^-, $4H_2O$ and one NCS^-. For each ligand, the donor atom is listed *first*.

What is the oxidation state of the transition metal ion?	**+3 or (III)**
What is the coordination number of the transition metal ion?	**6**
How many *d*-electrons in the transition metal ion?	**Cr is in group 6 so Cr(III) is d^3**
List all the ligand donor atoms.	**Cl^-, 4 × O and N**

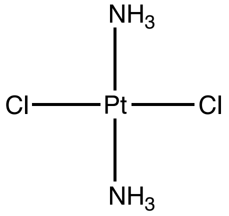
3

- Consider the complexes *cis*-$[PtCl_2(NH_3)_2]$ and *trans*-$[PtCl_2(NH_3)_2]$. Draw the structures of the two isomers, clearly illustrating the stereochemistry.

The platinum is bonded to four ligands (2 × Cl^- and 2 × NH_3). With four ligands, two geometries are possible – tetrahedral and square planar. Of these, only square planar gives rise to *cis* and *trans*-isomers and so the complexes must be square planar:



cis-diamminedichloridoplatinum(II)



trans-diamminedichloridoplatinum(II)

Briefly suggest why *cis*-[$PtCl_2(NH_3)_2$] is an effective anti-cancer drug, but *trans*-[$PtCl_2(NH_3)_2$] is not.

cis-[$PtCl_2(NH_3)_2$] is believed to act by binding the _cis_-$Pt(NH_3)_2$ group to two nearby nitrogen atoms on the bases of a strand of DNA. This can only be achieved by the _cis_ isomer – the _trans_ form has 180° between the vacant sites of the $Pt(NH_3)_2$ group and is not able to bind in this way.

The coordination of the platinum to the DNA causes a kink in the α-helix of the DNA and this prevents its replication.

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of V^{3+}. **1**

Paramagnetism is associated with the presence of unpaired electron spins. As vanadium is in group 5, V^{3+} has two electrons in its 3d orbitals. These electrons occupy separate orbitals with the same spin to reduce the repulsion between them:

↑	↑				**3*d***

V^{3+} thus has two unpaired electrons and is paramagnetic.

Marks
3

- Complete the following table. (en = ethylenediamine = $NH_2CH_2CH_2NH_2$)

Formula	$K_3[Fe(CN)_6]$	$[Cu(NH_3)_4(H_2O)_2](NO_3)_2$	*cis*-$[CrCl_2(en)_2]Cl$
Oxidation state of transition metal ion	**III or +3**	**II or +2**	**III or +3**
Coordination number of transition metal ion	**6** **($6 \times \underline{C}N^-$)**	**6** **($4 \times \underline{N}H_3 + 2 \times H_2\underline{O}$)**	**6** **($2 \times \underline{Cl^-} + 2 \times \underline{N}H_2CH_2CH_2\underline{N}H_2$)**
Number of *d*-electrons in the transition metal ion	**5**	**9**	**3**
Species formed upon dissolving in water	**$3K^+$** **$[Fe(CN)_6]^{3-}$**	**$[Cu(NH_3)_4(H_2O)_2]^{2+}$** **$2NO_3^-$**	***cis*-$[CrCl_2(en)_2]^+$** **Cl^-**

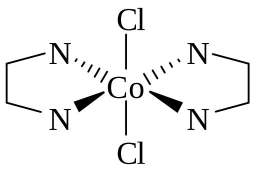
Marks
4

- What is a chelate ligand?

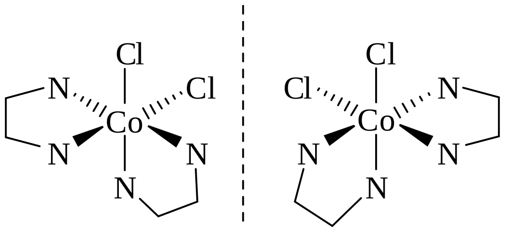
A chelate is a ligand with more than one donor atom that can bond to the same metal ion.

Draw all possible isomers of [$CoCl_2(en)_2$]. en = ethylenediamine = $NH_2CH_2CH_2NH_2$

***cis* and *trans* geometric isomers are possible. The *cis*-isomer can exist as non-superimposable mirror images (enantiomers).**



trans-



cis- ***cis-***

2

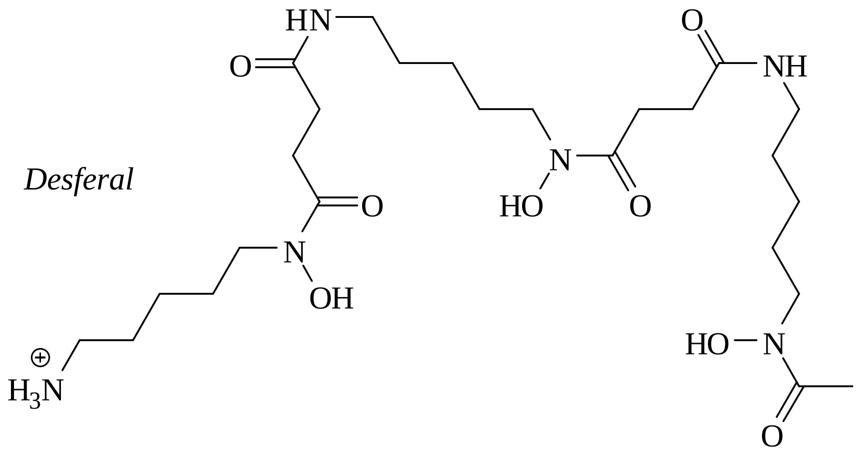
- Explain briefly why the [$Fe(H_2O)_6$]$^{3+}$ cation has a K_a of 6×10^{-3} M, whilst the [$Fe(H_2O)_6$]$^{2+}$ cation has a K_a of 4×10^{-9} M.

The Fe^{3+} ion has a higher charge and is smaller than the Fe^{2+} ion – it has a higher charge density. The higher charge density withdraws electron density from the oxygen and leading to a more polarised O–H bonds that are more easily broken.

Marks
3

- Hemochromatosis or "iron overload" is a potentially fatal disorder in which excess iron is deposited in the bodily organs as insoluble hydrated iron(III) oxide. It can be treated by administration of desferioxamine B (*Desferal*), a natural substance isolated from fungi.

Desferal



Desferal is taken over 8-12 hour periods up to six times per week. A value of log *K* = 30.6 is associated with the following equilibrium:

$$Fe^{3+} + LH_3^+ \rightleftharpoons FeL^+ + 3H^+ \quad \text{where } LH_3^+ = \textit{Desferal}$$

Briefly describe the chemical basis for the use of *Desferal* in iron overload therapy.

The solubility of Fe_2O_3 is *very* small - the equibrium for the reaction below lies far to the left:

$$Fe_2O_3(s) + \text{excess } H_2O \rightleftharpoons 2Fe^{3+}(aq) + 6OH^-(aq)$$

Complexation of Fe^{3+} ions with Desferal is very favourable – the equilibrium for the reaction below lies far to the right (as *K* for this reaction is $10^{30.6}$):

$$Fe^{3+} + LH_3^+ \rightleftharpoons FeL^+ + 3H^+ \quad \text{where } LH_3^+ = \textit{Desferal}$$

The Desferal complexes all free Fe^{3+}(aq) ions, so more Fe_2O_3 must dissolve to re-establish the first equilibrium (le Chatelier's principle). Eventually all the Fe_2O_3 will dissolve.

Marks
3

- Consider the compound with formula $[CoCl_2(NH_3)_4]Br\cdot 2H_2O$.

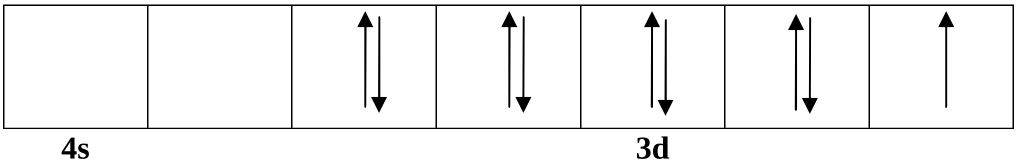
  Write the formula of the complex ion. **$[CoCl_2(NH_3)_4]^+$**

  Write the symbols of the ligand donor atoms. **Cl, N**

  What is the *d* electron configuration of the metal ion in this complex? **Co^{3+}: $3d^6$**

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of Cu^{2+}. 2

As Cu is in group 11, it has 11 valence electrons. Cu^{2+} therefore has (11 – 2) = 9. These occupy the five 3d orbitals:



There is an unpaired electron and so Cu^{2+} is paramagnetic.

- Complete the following table. 6

Formula	Oxidation state of transition metal	Coordination number of transition metal	Number of *d*-electrons in the transition metal	Species formed upon dissolving in water
$Na_2[CoCl_4]$	**+2**	**4**	**7**	**Na^+, $[CoCl_4]^{2-}$**
$[Ni(NH_3)_5(H_2O)]SO_4$	**+2**	**6**	**8**	**$[Ni(NH_3)_5(H_2O)]^{2+}$, SO_4^{2-}**
$[Cr(en)_3]Br_3$	**+3**	**6**	**3**	**$[Cr(en)_3]^{3+}$, Br^-**

en = ethylenediamine = $NH_2CH_2CH_2NH_2$