28. CHEMISTRY OF TRANSITION ELEMENTS

28.1 General Physical and Chemical Properties of the First Row of Transition Elements, Titanium to Copper

Define transition element.

- Element which forms one or more stable ions with incomplete d orbitals.

State the typical properties of transition elements

- variable oxidation states
- behave as catalysts
- form complex ions / complexes
- form coloured compounds / ions

Explain why transition elements have variable oxidation states.

- Energies / energy levels of the 3d and the 4s (sub-shells / orbitals) are similar OR the difference between the 3d and the 4s is small.

Explain why transition elements can form complex ions.

- They have vacant d orbitals that are energetically accessible.

Explain why transition elements behave as catalysts.

- more than one (stable) oxidation state.
- empty / vacant (d) orbitals are energetically accessible OR empty / vacant (d) orbitals can form dative bonds with ligands.

Define degenerate d orbitals.

- Orbitals are at the same energy.

Hydrated compound **J**, $K_3Fe(C_2O_4)_3{\bullet}xH_2O$, contains the green complex ion $[Fe(C_2O_4)_3]^{3-}$.

The value of *x* can be determined by titration of a sample of **J** with acidified MnO_4^- ions.

MnO_4^- ions oxidise $C_2O_4^{2-}$ ions in acidic conditions.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

A student prepares a solution containing 0.100 g of **J**.

The student titrates this solution with 0.0200 mol dm^{-3} acidified $KMnO_4$(aq). The titre obtained is 12.20 cm^3.

Assume all of the $C_2O_4^{2-}$ ions are oxidised.

Calculate the value of *x* in $K_3Fe(C_2O_4)_3 \cdot xH_2O$.

Give your answer to the nearest whole number. Show your working.

[M_r: $K_3Fe(C_2O_4)_3$, 437.1]

M1 moles of manganate	= 12.20 / 1000 × 0.0200	= 2.44 × 10^{-4} mol
AND moles of ethanedioate	= 5 / 2 × 2.44 × 10^{-4}	= 6.10 × 10^{-4} mol
M2 moles of $K_3Fe(C_2O_4)_3$	= 6.10 × 10^{-4} ÷ 3	= 2.03 × 10^{-4} mol
AND mass of $K_3Fe(C_2O_4)_3$	= 437.1 × 2.03 × 10^{-4}	= 0.0889 g
M3 mass of water	= 0.100 – 0.0889	= 0.0111 g
AND moles of water	= 0.0111 / 18.0	= 6.18 × 10^{-4} mol
M4 *x* = molar ratio	= 6.18 × 10^{-4} / 2.03 × 10^{-4}	= 3

NOTE: follow this working!!

An excess of concentrated HC*l* is added to a solution containing $[Co(H_2O)_6]^{2+}$.

Describe the colour change observed and the state of the cobalt-containing product.

The colour changes from .... to ....

The state of the cobalt-containing product is ....

- Pink to blue
- State= aqueous

Write an equation for the reaction occurring above.

$[Co(H_2O)_6]^{2+} + 4HCl \rightarrow [CoCl_4]^{2-} + 6H_2O + 4H^+$ **OR** $[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$

Write an equation for the reaction that occurs when an excess of NaOH(aq) is added to a solution containing [Co(H2O)6]2+

$[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow Co(OH)_2(H_2O)_4 + 2H_2O$ **OR**
$[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow Co(OH)_2 + 6H_2O$

28.2 General Characteristic Chemical Properties of the First Set of Transition Elements, Titanium to Copper

Define complex

- A molecule or ion formed by a central metal / transition element atom / ion surrounded / bonded by one or more ligands.

Explain what is meant by a polydentate ligand.

- a species that donates more than two lone pairs.
- to form dative / coordinate bonds to a metal atom or ion.

State what is meant by coordination number

- The number of coordinate bonds being formed by the metal atom/ ion.

The H—O—H bond angle in water is 104.5°. Suggest the H—O—H bond angle in $[Fe(H2O)6]^{3+}$. Explain your answer.

- 106˚-108˚
- Lone pair from O is donated in a bond OR one more of O's electron pairs is now a bond/bonding pair (so repels less).

$[Fe(H_2O)_5(H_2PO_4)]^{2+}$ can form when H_3PO_4 reacts with $[Fe(H_2O)_6]^{3+}$. Write an equation for this reaction.

- $[Fe(H_2O)_6]^{3+} + \mathbf{H_3PO_4} \rightarrow [Fe(H_2O)_5(H_2PO_4)]^{2+} + H_3O^+$

2 different complex ions, X and Y, can form when anhydrous RuCl3 reacts with water under certain conditions. X and Y have octahedral geometry.
Aqueous samples of X and Y react separately with an excess of AgNO3(aq). Different amounts of AgCl are precipitated:

- **1 mole of complex ion X produces 2 moles of AgCl**
- **1 mole of complex ion Y produces 1 mole of AgCl.**

Suggest formulae for X and Y.

X	$[Ru(H_2O)_5Cl]^{2+}$
Y	$[Ru(H_2O)_4Cl_2]^{+}$

- For 2 mol AgCl to be produced, complex ion must have +2 charge, and for 1 mol AgCl, it has to have +1 charge.
- To deduce formula of complex ion from moles of AgCl ppt formed – look at the charge NOT the number of Cl atoms.

$$\mathrm{RuCl_3} + 5H_2O \longrightarrow [RuCl(H_2O)_5]Cl_2$$

$$2Cl^- + 2Ag^+ \longrightarrow 2AgCl$$

$$\mathrm{RuCl_3} + 4H_2O \longrightarrow [RuCl_2(H_2O)_4]Cl$$

$$Cl^- + Ag^+ \longrightarrow AgCl$$

Samples of $[Cu(H_2O)_6]^{2+}$(aq) are reacted separately with an excess of solution **A** and with an excess of solution **B**.

The reaction of $[Cu(H_2O)_6]^{2+}$(aq) with solution **A** is a precipitation reaction.

The reaction of $[Cu(H_2O)_6]^{2+}$(aq) with solution **B** is a ligand substitution reaction.

Suggest a possible identity for solution **A** and for solution **B**. Give relevant observations and the formula of the copper-containing product for each reaction.

- precipitation solution **A**: e.g. NaOH / OH^-
- observations: (pale) blue ppt. / solid
- product: $Cu(OH)_2$ **OR** $[Cu(OH)_2(H_2O)_4]$ ecf from **A**

- ligand substitution solution **B**: e.g. HCl / Cl^-, NH_3
- observations: dark/deep blue solution (with NH_3) **OR yellow** solution (with Cl^-)
- product: $[Cu(NH_3)_4(H_2O)_2]^{2+}$ **OR** $[CuCl_4]^{2-}$

Explain what is meant by a bidentate ligand

- Species with 2 lone pairs of electrons
- that form dative (covalent) / co-ordinate bond(s) to central metal atom / ion

Name the shape of the complex ion $[Ag(NH_3)_2]^+$.

- Linear

State the bond angle for H-N-Ag and for N-Ag-N in $[Ag(NH_3)_2]^+$.

- H-N-Ag = 109.5˚
- N-Ag-N = 180˚

Suggest how pyrazine is able to bond to two separate ruthenium ions.

pyrazine

- Has a lone pair on each N atom / two lone pairs on the N atoms, which can be donated / form a coordinate / dative bond (with Ru).

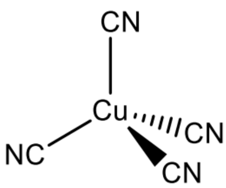
reagent added to $[Co(H_2O)_6]^{2+}(aq)$	**cobalt-containing species formed**
NaOH(aq)	$[Co(H_2O)_4(OH)_2]$
an excess of NH3(aq)	$[Co(NH_3)_6]^{2+}$
an excess of conc. HCl(aq)	$[CoCl_4]^{2-}$

- original colour of $[Co(H_2O)_6]^{2+}(aq)$ = pink
- final colour after addition of an excess of conc. HCl(aq) = blue

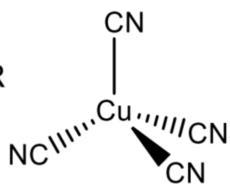
Silver forms the linear complex ion [Ag(CN)2]–. Copper forms the tetrahedral complex ion [Cu(CN)4]3–. Draw three-dimensional diagrams to show the shapes of these complex ions. Label one bond angle on each diagram.

bond angle must go from bond to bond
OR CN group to CN group
diagram

- for Ag: NC—Ag—CN
- angle = labelled 180°



OR



- for Cu:
- angle = labelled 109–110°

any two [1] all four [2]

A piece of a copper-containing alloy has a mass of 0.567 g. It is dissolved in an acid giving 100.0 cm^3 of a blue solution in which all the copper is present as Cu^{2+} ions.

An excess of KI(aq) is added to a 25.0 cm^3 sample of this solution.

All of the copper is precipitated as white CuI(s).

Cu^{2+} ions are the only component in the solution that react with KI(aq). This is reaction 1.

reaction 1 $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$

The liberated I_2 is then titrated with 0.0200 mol dm^{-3} $S_2O_3^{2-}$. This is reaction 2.

reaction 2 $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

The titration requires 20.10 cm^3 of 0.0200 mol dm^{-3} $S_2O_3^{2-}$ to reach the end-point.

(i) Calculate the number of moles of I_2 that are reduced in this titration.

number of moles of I_2 = ... mol [1]

(ii) Calculate the number of moles of copper in the original piece of alloy.

number of moles of copper = ... mol [1]

(iii) Calculate the percentage of copper in the alloy.

percentage of copper = ... % [1]

mol of I_2 = $0.5 \times 0.02 \times 20.1 / 1000 = 2.01 \times 10^{-4}$ [1] min 2sf
mol of Cu = $2.01 \times 10^{-4} \times 2 \times 4 = 1.608 / 1.61 \times 10^{-3}$ [1] ecf min 2sf
% of Cu = $100 \times (1.608 \times 10^{-3} \times 63.5) / 0.567 = 18.0$ [1] ecf

The concentration of Cu2+(aq) in a solution can be determined by the reaction of Cu2+ ions with I– ions. The I2 produced in reaction 1 is titrated against a solution containing thiosulfate ions, S2O32–, using a suitable indicator.
Identify a suitable indicator for the titration.

- Starch indicator

NOTE: starch indicator forms blue-black complex with elemental iodine (I2).

Give the electronic configuration of an isolated Ti3+ ion.

- $(1s^2)\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ (4s^0)$

REMEMBER:

- 4s fills up first, and electrons are removed from it first.
- Chromium and copper have 4s1.

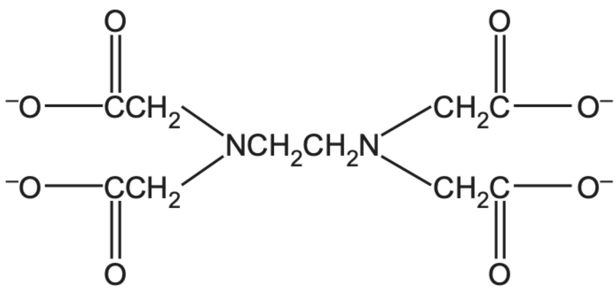
Group 2 metal ions can form complexes similar to those of transition elements.

A solution of $EDTA^{4-}$ is added to water containing $[Ca(H_2O)_6]^{2+}$ to form a new complex, $[CaEDTA]^{2-}$, as shown.

equilibrium 1 $[Ca(H_2O)_6]^{2+} + EDTA^{4-} \rightleftharpoons [CaEDTA]^{2-} + 6H_2O$

Circle on the structure of $EDTA^{4-}$ in Fig. 1.2 the **six** atoms that form bonds with the metal ion.

$EDTA^{4-}$



- six atoms circled: 2N and 4O from different CO2.

The complex $[CaEDTA]^{2-}$ can be used to remove toxic metals from the body.

Table 1.2 shows the numerical values for the stability constants, K_{stab}, for some metal ions with $EDTA^{4-}$.

Table 1.2

complex	K_{stab}
$[CaEDTA]^{2-}$	5.0×10^{10}
$[CrEDTA]^{-}$	2.5×10^{23}
$[FeEDTA]^{-}$	1.3×10^{25}
$[PbEDTA]^{2-}$	1.1×10^{18}

An aqueous solution containing $[CaEDTA]^{2-}$ is added to a solution containing equal concentrations of Cr^{3+}(aq), Fe^{3+}(aq) and Pb^{2+}(aq). The resulting mixture is left to reach a state of equilibrium.

State the type of reaction when [CaEDTA]2– reacts with Cr3+(aq), Fe3+(aq) and Pb2+(aq).

- ligand exchange

The number of moles of water of crystallisation in a hydrated ionic salt can be determined by titration using aqueous $EDTA^{4-}$ ions with a suitable indicator.

- 0.255 g of hydrated chromium(III) sulfate, $Cr_2(SO_4)_3 \bullet nH_2O$, is dissolved in water and made up to 100 cm^3 in a volumetric flask.
- 25.0 cm^3 of this solution requires 26.2 cm^3 of 0.00800 mol dm^{-3} aqueous $EDTA^{4-}$ ions to reach the end-point.

The reaction occurs as shown.

$$[Cr(H_2O)_6]^{3+} + EDTA^{4-} \rightarrow [CrEDTA]^{-} + 6H_2O$$

Use the data to calculate the value of n in the formula of $Cr_2(SO_4)_3 \bullet nH_2O$.

Show your working.

Use the data to calculate the value of *n* in the formula of $Cr_2(SO_4)_3 \cdot nH_2O$.

Show your working.

mol of $EDTA^{4-}$ $= \frac{26.2}{1000} \times 0.008 = 2.096 \times 10^{-4}$ ✓

for 100 cm³ soln : $2.096 \times 10^{-4} \times 4 = 8.384 \times 10^{-4}$ of $[Cr(H_2O)_6]^{3}$

mol of $Cr_2(SO_4)_3 \cdot nH_2O = \frac{8.384 \times 10^{-4}}{2} = 4.192 \times 10^{-4}$ ✓

$0.255 = 4.192 \times 10^{-4} (392.3 + 18n)$

$n = \frac{0.255 - 4.192 \times 10^{-4} \times 392.3}{4.192 \times 10^{-4} \times 18} = 12$

✓

n = ...12.. [3] 3

The complexes $[Pt(NH_3)_2Cl_2]$ and $[Pt(en)_2]^{2+}$ have the same geometry (shape) around the metal ion. $[Pt(NH_3)_2Cl_2]$ exists as two stereoisomers, whereas $[Pt(en)_2]^{2+}$ only has one possible structure.
State the geometry around the metal ion.

- Square planar

NOTE: you should know this compound. Cisplatin OR transplatin. It always has square planar geometry.

The reaction of iodine and hot aqueous sodium hydroxide is similar to that of chlorine and hot aqueous sodium hydroxide. Sodium iodate, NaIO3, is formed as one of the products. Suggest an equation for the reaction of iodine and hot aqueous sodium hydroxide.

$3I_2 + 6NaOH \rightarrow NaIO_3 + 5NaI + 3H_2O$

When an excess of NH3 (aq) is added to a solution of [CuCl4]2−(aq), [Cu(NH3)4(H2O)2]2+(aq) is formed. Write an equation for the reaction.

$[CuCl_4]^{2-} + 4NH_3 + 2H_2O \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4Cl^-$

Remember to write the 2H2O as a reactant.

28.3 Colour of Complexes

$[Cu(H_2O)_6]^{2+}$	pale blue	$[Co(H_2O)_6]^{2+}$	pink
$Cu(H_2O)_4(OH)_2$	pale blue	$Co(H_2O)_4(OH)_2$	blue
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	deep/ dark blue	$[Co(NH_3)_6]^{2+}$	brown
$CuCl_4^{2-}$	yellow	$CoCl_4^{2-}$	blue

$Cu(NO_3)_2$ is added to water to form solution **A**.
Fig. 1.1 shows some reactions of solution **A**.

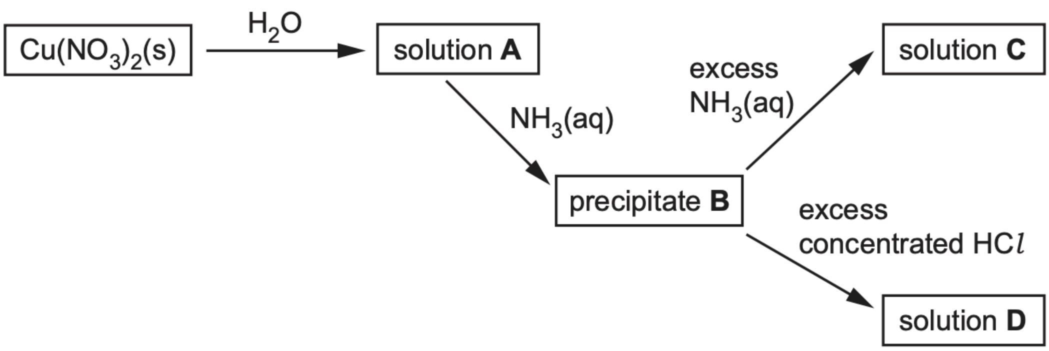


Fig. 1.1

Complete Table 1.1 to show the formula and colour of each of the copper-containing species present in **A**, **B**, **C** and **D**.

Table 1.1

	formula of copper-containing species formed	colour of copper-containing species formed
A		
B		
C		
D		

copper-containing species	formula of copper-containing species formed	colour copper-containing formed
A	$[Cu(H_2O)_6]^{2+}$	(pale) blue
B	$Cu(H_2O)_4(OH)_2$ ***or*** $Cu(OH)_2$	(pale) blue
C	$[Cu(NH_3)_4(H_2O)_2]^{2+}$	**dark** blue
D	$CuCl_4^{2-}$	yellow

Explain why transition elements can form coloured complexes.

- d orbitals of different energy / d-d splitting occurs
- electrons promoted / excited
- light / wavelength / frequency / photon is absorbed AND complementary colour seen

TiO2+(aq) is a colourless ion. Suggest why.

- Ti is in +4 oxidation state, so no d electrons OR Ti in TiO2+ has no d electrons.
- cannot absorb photons/light in visible spectrum OR no wavelength/frequency absorbed in visible spectrum.

A solution of Cr3+(aq) and a solution of Fe3+(aq) have different colours. Explain why the two complexes have different colours.

- d–d energy gap / ΔE is different
- different frequency (of light) is absorbed

Explain why [Ag(NH3)2]+ complexes are colourless.

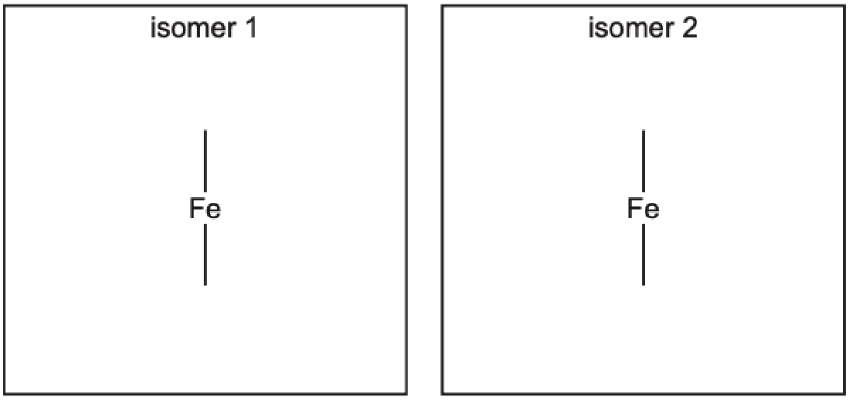
- d-subshell is full / complete OR d10 OR d-orbitals are full
- No d-d transition OR no d electrons promoted/excited

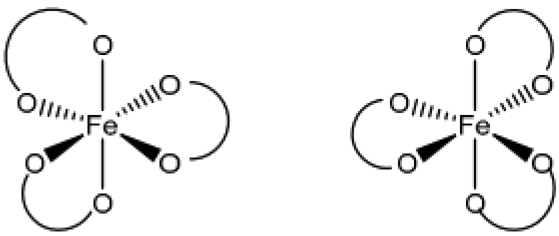
28.4 Stereoisomerism in Transition Elements

The $[Fe(C_2O_4)_3]^{3-}$ complex ion shows stereoisomerism.

Complete the three-dimensional diagrams in Fig. 3.1 to show the **two** stereoisomers of $[Fe(C_2O_4)_3]^{3-}$.

The $C_2O_4^{2-}$ ligand can be represented using .





- When drawing out optical isomers, only make them exact mirror images of each other. Let the bonds point in the same direction.

(iv) Ti(acac)$_2$Cl_2 shows both optical and geometrical (cis/trans) isomerism.

Ti(acac)$_2$Cl_2 exists as three stereoisomers.

The structure of one stereoisomer of Ti(acac)$_2$Cl_2 is shown in Fig. 3.2.

stereoisomer 1

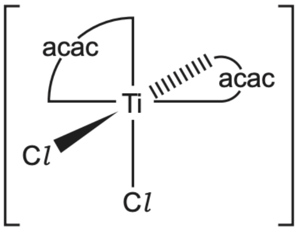
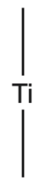


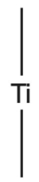
Fig. 3.2

Complete the structures of the other two stereoisomers of Ti(acac)$_2$Cl_2.

stereoisomer 2

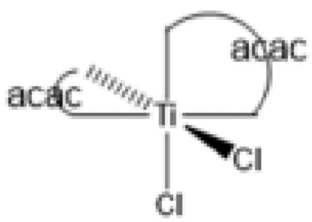


stereoisomer 3

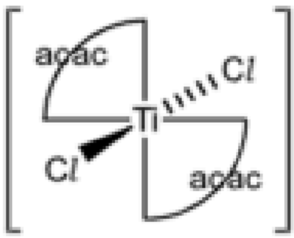


[2]

mirror image of isomer **I**



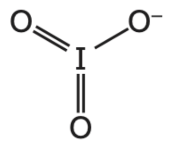
trans isomer



The acac– anion is symmetrical. Deduce which, if any, of stereoisomers 1, 2 and 3 in (iv) are polar. Explain your answer.

- isomer I AND cis isomer drawn by candidate.
- dipoles do not cancel.

The IO_3^- anion is shown.

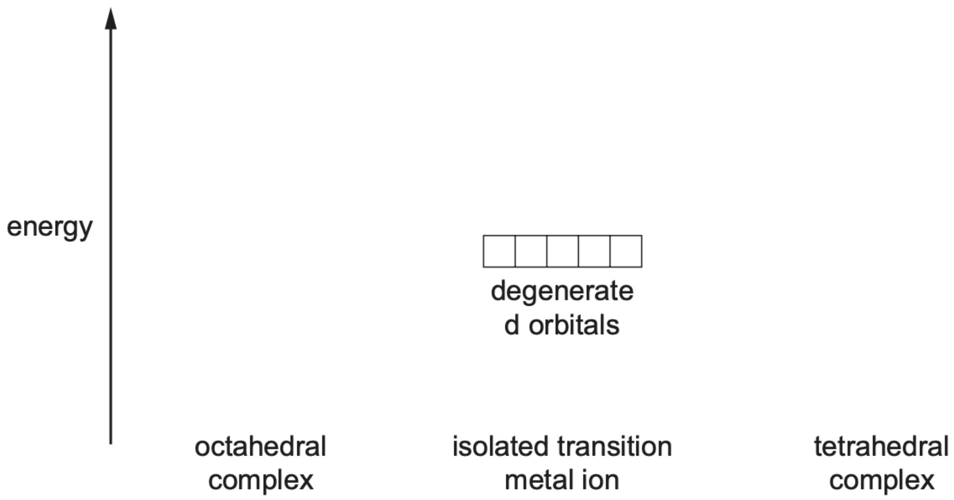


Explain, with reference to the qualitative model of electron-pair repulsion, why the IO3– anion has a pyramidal shape.

- 3 bonding-pair centres AND 1 lone pair of electrons on iodine.

The d orbitals in an isolated transition metal ion are degenerate. In complexes, the d orbitals occupy two energy levels.

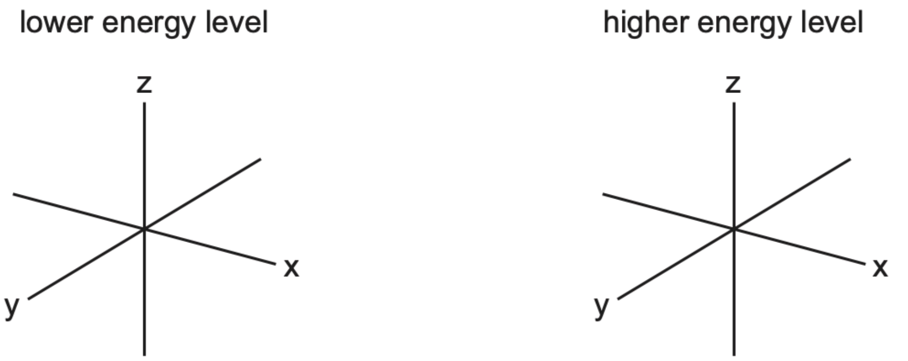
(i) Complete the diagram to show the arrangement of d orbital energy levels in octahedral and in tetrahedral complexes.



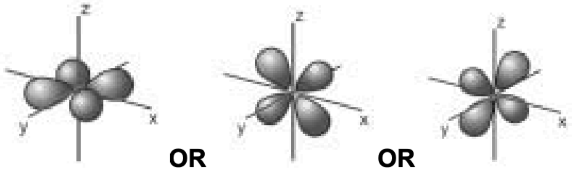
(ii) Sketch the shape of **two** d orbitals:

- one d orbital from the lower energy level in an octahedral complex
- one d orbital from the higher energy level in an octahedral complex.

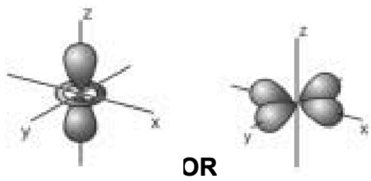
Use the axes below.



M1: *lower energy level (in between axes)*



M2: *higher energy level (on the axes)*



28.5 Stability Constants

Define the stability constant of a complex.

- equilibrium constant for the formation of the complex (ion)
- in a solvent / water / solution OR from its constituent ions or molecules

Complete the expression for the K_{stab} of $[Cd(CH_3NH_2)_4]^{2+}$.

K_{stab} =

Ans:

$$\frac{[[Cd(CH_3NH_2)_4]^{2+}]}{[Cd^{2+}][CH_3NH_2]^4}$$

- First write down the balanced equation for the formation.
- Then do product/reactant.
- Remember to raise to the power 4!!! To the power of stoichiometric coefficient!!