

- Ethylenediamine tetraacetate (EDTA^{4-}) is a ligand that forms complexes with many metal ions and consequently may be used to treat heavy metal toxicity in the body. The reaction with lead ions is represented by the following equilibrium:



If a solution had an initial concentration of $1 \times 10^{-4} \text{ M Pb}^{2+}$ and 0.05 M EDTA , what will be the concentration of uncomplexed lead ions once equilibrium is established? K_{stab} for $[\text{PbEDTA}]^{2-}$ is $1 \times 10^{18} \text{ M}^{-1}$.

K_{stab} is very large so the amount of uncomplexed Pb^{2+} will be tiny.

If $[\text{Pb}^{2+}] = x \text{ M}$,

$$[[\text{PbEDTA}]^{2-}] = (1 \times 10^{-4} - x) \text{ M} \sim 1 \times 10^{-4} \text{ M as } x \text{ is so small.}$$

$$[\text{EDTA}^{4-}] = 0.05 - (1 \times 10^{-4} - x) \text{ M} \sim 0.05 - (1 \times 10^{-4}) \text{ M} = 0.0499 \text{ M}$$

Hence,

$$K_{\text{stab}} = \frac{[[\text{PbEDTA}]^{2-}]}{[\text{Pb}^{2+}][\text{EDTA}^{4-}]} = \frac{(1 \times 10^{-4})}{x(0.0499)} = 1 \times 10^{18}$$

$$x = [\text{Pb}^{2+}] \text{ M} = 2 \times 10^{-21} \text{ M}$$

Answer: $[\text{Pb}^{2+}] = 2 \times 10^{-21} \text{ M}$

- Briefly outline three kinds of isomerism that can arise in coordination complexes, illustrating each type of isomerism with structural formulas. Give the systematic name for any one of your structures.

Structural isomers have the atoms connected differently:

- (i) **coordination isomers have different ligands attached. For example, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ can potentially exist as:**

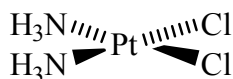
$[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$	hexaqua chromium(III) chloride
$[\text{CrCl}(\text{OH}_2)_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$	pentaquachlorido chromium(III) chloride-1-water
$[\text{CrCl}_2(\text{OH}_2)_4]\text{Cl} \cdot 2\text{H}_2\text{O}$	tetraquachlorido chromium(III) chloride-2-water
$[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$	triaquachlorido chromium(III) chloride-3-water

- (ii) **linkage isomers have different atoms on a ligand attached. For example, NO_2^- can bond through the N atom, to make nitro complexes, or through an O atom, to make nitrito complexes:**

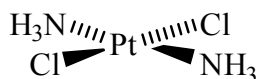
$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$	pentamminenitro cobalt(III) chloride
$[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$	pentaaminenitrito cobalt(III) chloride

Stereoisomers have the atoms connected in the same way but have different spatial arrangements:

- (i) **geometrical isomers have different arrangements in space. Examples include *cis* and *trans* isomers such as those of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$:**

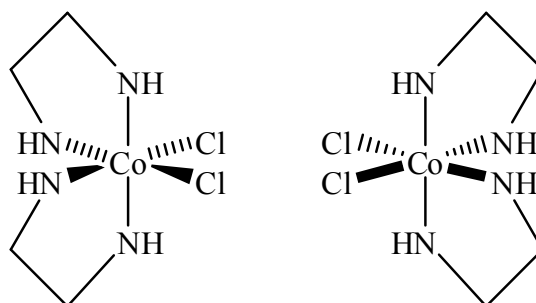


cis-diamminedichloridoplatinum(II)



trans-diamminedichloridoplatinum(II)

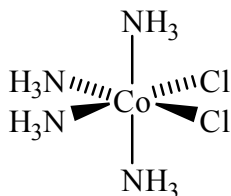
- (ii) **optical isomers are non-superimposable mirror images. For example, the *cis* isomer of $[\text{CoCl}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2](\text{NO}_3)$ can exist in two forms**



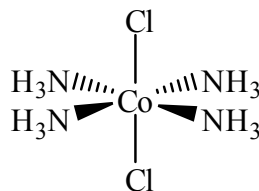
dichloridobis(ethylenediamine)cobalt(III) nitrate

- Coordination complexes can display a number of types of isomerism. Draw a simple diagram showing a pair of geometric isomers. Label your diagram with the systematic name of each isomer.

The compound $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$ can exist as in two isomeric forms which differ in the arrangement of the ligands in space.



***cis*-tetraamminedichloridocobalt(II)**



***trans*-tetraamminedichloridocobalt(II)**

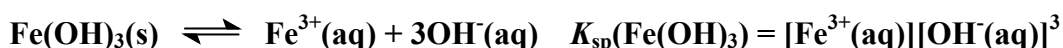
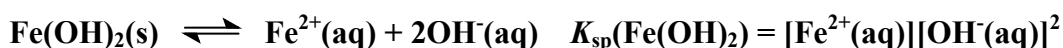
Marks
4

- The presence of iron in inorganic qualitative analysis is detected by the precipitation of the hydroxide using a buffer of pH 8. The solubility product constant of $\text{Fe}(\text{OH})_3$ is $4 \times 10^{-38} \text{ M}^4$ and that of $\text{Fe}(\text{OH})_2$ is $4 \times 10^{-15} \text{ M}^3$. Is it more sensible to try and detect the presence of Fe^{2+} ions or Fe^{3+} ions? Show all working and then give a reason for your answer.

Using $\text{pOH} = -\log_{10}([\text{OH}^-(\text{aq})])$ and $\text{pH} + \text{pOH} = 14.0$:

$$\text{pOH} = (14.0 - 8.0) = 6.0 \text{ and} \\ [\text{OH}^-(\text{aq})] = 1 \times 10^{-6} \text{ M}$$

The solubility equilibria and products are :



Hence,

$$[\text{Fe}^{2+}(\text{aq})] = \frac{K_{\text{sp}}(\text{Fe}(\text{OH})_2)}{[\text{OH}^-(\text{aq})]^2} = \frac{(4 \times 10^{-15})}{(1.0 \times 10^{-6})^2} = 4 \times 10^{-3} \text{ M}$$

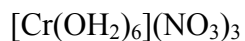
$$[\text{Fe}^{3+}(\text{aq})] = \frac{K_{\text{sp}}(\text{Fe}(\text{OH})_3)}{[\text{OH}^-(\text{aq})]^3} = \frac{(4 \times 10^{-38})}{(1.0 \times 10^{-6})^3} = 4 \times 10^{-20} \text{ M}$$

As $\text{Fe}(\text{OH})_2(\text{s})$ $\text{Fe}(\text{OH})_3(\text{s})$ dissolves to give 1 $\text{Fe}^{2+}(\text{aq})$ and 1 $\text{Fe}^{3+}(\text{aq})$, these are also the molar solubilities.

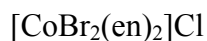
The solubility of $\text{Fe}(\text{OH})_3$ is much lower so it will precipitate at much lower iron concentrations. It is therefore easier to detect Fe^{3+} .

2

- Name the following complexes.



hexaaquachromium(III) nitrate

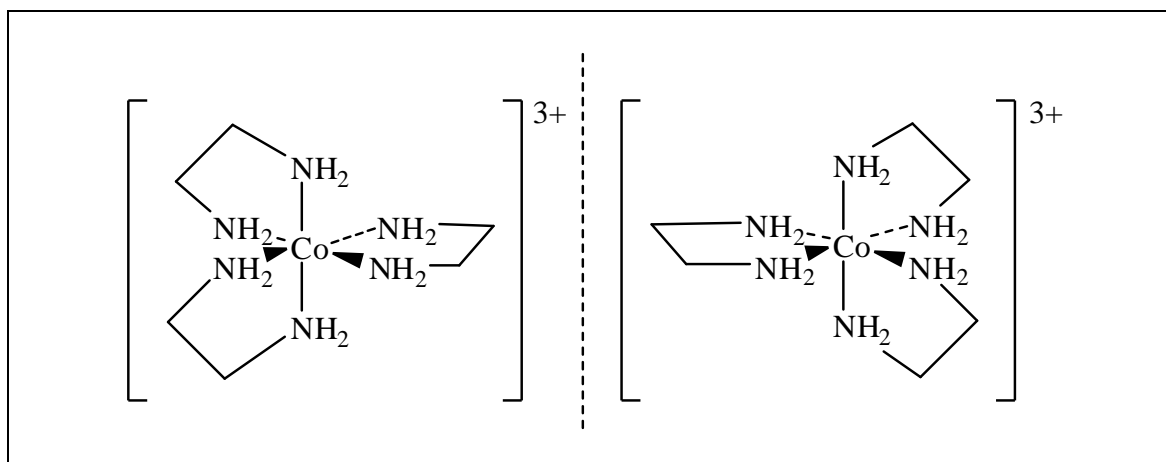


dibromidobis(ethylenediamine)cobalt(III) chloride

en = ethylenediamine = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

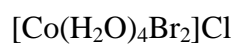
2

- Draw all stereoisomers of the complex ion of $[\text{Co}(\text{en})_3]\text{Br}_3$.
(en = ethylenediamine = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$)

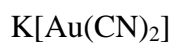


2

- Name the following complexes.

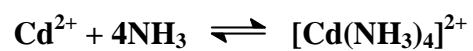


tetraaquadibromocobalt(III) chloride



potassium dicyanoaurate(I)

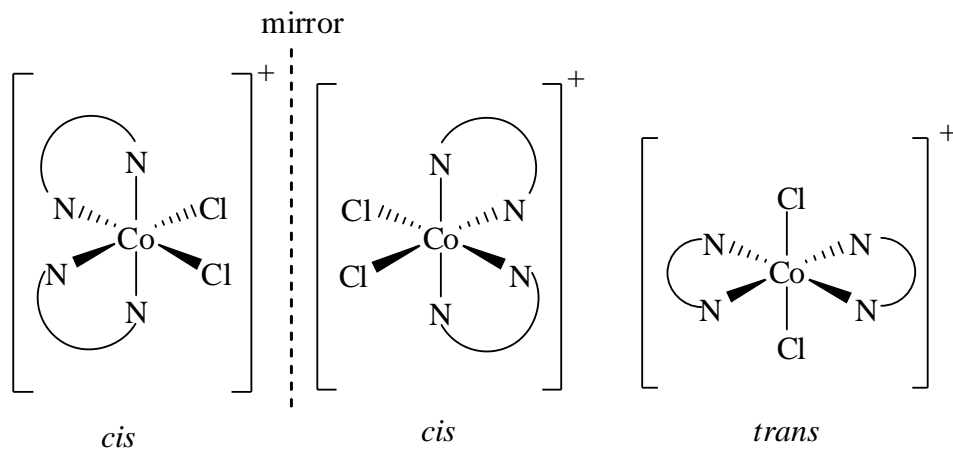
- Write the chemical equation for the formation of the complex ion $[\text{Cd}(\text{NH}_3)_4]^{2+}$.

Marks
2

Write the associated stability constant expression (K_{stab}).

$$K_{\text{stab}} = \frac{[[\text{Cd}(\text{NH}_3)_4]^{2+}]}{[\text{Cd}^{2+}][\text{NH}_3]^4}$$

- Draw all possible stereoisomers of the complex ion $[\text{CoCl}_2(\text{en})_2]^+$. Label each as *cis* or *trans*.

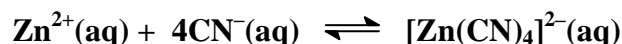


dichlorobisethylenediaminecobalt(III) ion

The *cis* isomer is non-superimposable on its mirror image whereas the *trans* isomer is not chiral.

- Zinc sulfate (8.07 g) is dissolved in 1.00 L of a 1.00 M solution of KCN. Write the chemical equation for the formation of the aqueous ion $[\text{Zn}(\text{CN})_4]^{2-}$.

Marks
4



Calculate the concentration of $\text{Zn}^{2+}(\text{aq})$ in solution at equilibrium. Ignore any change in volume upon addition of the salt. K_{stab} of $[\text{Zn}(\text{CN})_4]^{2-} = 4.2 \times 10^{19} \text{ M}^{-4}$.

The formula mass of zinc sulfate (ZnSO_4) is:

$$\text{formula mass} = 65.39 (\text{Zn}) + 32.07 (\text{S}) + 4 \times 16.00 (\text{O}) = 161.46 \text{ g mol}^{-1}$$

The number of moles in 8.07 g is therefore:

$$\text{number of moles} = n = \frac{m}{M} = \frac{8.07 \text{ g}}{161.46 \text{ g mol}^{-1}} = 0.0500 \text{ mol}$$

As $c = \frac{n}{V}$, $[\text{Zn}^{2+}(\text{aq})]_{\text{initial}} = 0.0500 \text{ M}$ when this is dissolved in a 1.00 L solution.

The reaction table is:

	$\text{Zn}^{2+}(\text{aq})$	$4\text{CN}^{-}(\text{aq})$	\rightleftharpoons	$[\text{Zn}(\text{CN})_4]^{2-}(\text{aq})$
initial	0.0500	1.00		0
change	-x	-4x		+x
equilibrium	0.0500 - x	1.00 - 4x		x

As K_{stab} is *very* large, virtually all of the $\text{Zn}^{2+}(\text{aq})$ will have reacted. It is a good approximation, therefore, to take:

$$[\text{CN}^{-}(\text{aq})]_{\text{equilibrium}} = 1.00 - 4x \sim 1.00 - 4 \times [\text{Zn}^{2+}(\text{aq})]_{\text{initial}} \\ = (1.00 - 4 \times 0.0500) \text{ M} = 0.80 \text{ M}$$

$$[[\text{Zn}(\text{CN})_4]^{2-}(\text{aq})]_{\text{equilibrium}} = x \sim [\text{Zn}^{2+}(\text{aq})]_{\text{initial}} \\ = 0.0500 \text{ M}$$

At equilibrium,

$$K_{\text{stab}} = \frac{[[\text{Zn}(\text{CN})_4]^{2-}(\text{aq})]}{[\text{Zn}^{2+}(\text{aq})][\text{CN}^{-}(\text{aq})]^4} = \frac{0.0500}{(0.0500 - x)(0.80)^4} = 4.2 \times 10^{19}$$

Hence, $[\text{Zn}^{2+}(\text{aq})]_{\text{equilibrium}} = (0.0500 - x) \text{ M} = 2.9 \times 10^{-21} \text{ M}$

Answer: $2.9 \times 10^{-21} \text{ M}$

Name the complex ion.

tetracyanozincate(II) ion

Marks
5

- Cisplatin, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, is a particularly effective chemotherapy agent against certain types of cancer. Calculate the concentration of $\text{Pt}^{2+}(\text{aq})$ ions in solution when 0.075 mol of cisplatin is dissolved in 1.00 L of a 1.00 M solution of NH_3 . K_{stab} of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2] = 3.4 \times 10^{12}$.

The initial concentration of cisplatin when 0.075 mol is dissolved in 1.00 L is 0.075 M.

As K_{stab} refers to the formation of the complex, the reaction table is:

	$\text{Pt}^{2+}(\text{aq})$	$2\text{Cl}^-(\text{aq})$	$2\text{NH}_3(\text{aq})$	\rightleftharpoons	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
Initial	0	0	1.00		0.075
Change	+x	+2x	+2x		-x
Equilibrium	x	2x	1.00 + 2x		0.075 - x

Hence:

$$K_{\text{stab}} = \frac{[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]}{[\text{Pt}^{2+}][\text{Cl}^-]^2[\text{NH}_3]^2} = \frac{(0.075-x)}{(x)(2x)^2(1.00+2x)^2} = 3.4 \times 10^{12}$$

As K_{stab} is so large, x will be very, very small and so $(1.00 + 2x) \sim 1.00$ and $(0.075 - x) \sim 0.075$. With this:

$$K_{\text{stab}} \sim \frac{(0.075)}{(x)(2x)^2(1.00)^2} = \frac{(0.075)}{(4x)^3} = 3.4 \times 10^{12}$$

$$x = [\text{Pt}^{2+}(\text{aq})] = 1.8 \times 10^{-5} \text{ M}$$

Answer: $1.8 \times 10^{-5} \text{ M}$

What changes would occur to the values of K_{stab} for cisplatin and the concentration of $\text{Pt}^{2+}(\text{aq})$ ions if solid KCl were dissolved in the above solution?

K_{stab}	increase	<u>no change</u>	decrease
$[\text{Pt}^{2+}(\text{aq})]$	increase	no change	<u>decrease</u>

- K_{stab} is the stability constant – it is a constant at any given temperature.
- From Le Chatelier's principle, if $[\text{Cl}^-(\text{aq})]$ is increased then the equilibrium will shift to the right and so $[\text{Pt}^{2+}(\text{aq})]$ will decrease.

- The general formula for a nickel(II) chloride compound complexed with ammonia is $[\text{Ni}(\text{NH}_3)_x]\text{Cl}_2$. A 0.59 g sample of the salt was dissolved in water and the ammonia from it was titrated with 153 mL of 0.100 M HCl. What is the value of the coefficient x ?

The molar mass of $[\text{Ni}(\text{NH}_3)_x]\text{Cl}_2$ is:

$$\begin{aligned} & (58.69 \text{ (Ni)} + x (14.01 \text{ (N)} + 3 \times 1.008 \text{ (H)}) + 2 \times 35.45 \text{ (Cl)}) \text{ g mol}^{-1} \\ & = (129.59 + 17.034x) \text{ g mol}^{-1} \end{aligned}$$

A 0.59 g sample therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{0.59}{(129.59 + 17.034x)} \text{ mol} \quad (1)$$

The number of moles in 153 mL of 0.100 M HCl is:

$$\begin{aligned} \text{number of moles} &= \text{concentration} \times \text{volume} \\ &= 0.100 \text{ mol L}^{-1} \times 0.153 \text{ L} = 0.0153 \text{ mol} \end{aligned}$$

Ammonia reacts with HCl according to the reaction $\text{NH}_3 + \text{HCl} \rightleftharpoons \text{NH}_4\text{Cl}$ and so this is equal to the number of moles of NH_3 present. Each mol of $[\text{Ni}(\text{NH}_3)_x]\text{Cl}_2$ contains x mol of NH_3 so the number of moles of $[\text{Ni}(\text{NH}_3)_x]\text{Cl}_2$ is:

$$\text{number of moles} = 0.0153 / x \text{ mol} \quad (2)$$

The value of x is calculated by equating (1) and (2). This is easiest to achieve by trial and error.

x	(1) / mol	(2) / mol
1	0.0040	0.015
2	0.0036	0.0077
3	0.0033	0.0051
4	0.0030	0.0038
5	0.0027	0.0031
6	0.0026	0.0026
7	0.0024	0.0022

The best agreement is for $x = 6$ - a common coordination number for Ni(II).

Answer: 6