Marks

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

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 ($[Fe(OH_2)_6]^{2+}$).

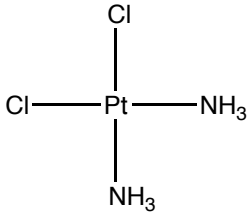
As pK_a = -$\log_{10}K_a$, a higher K_a means a *lower* pK_a. Thus, $[Fe(OH_2)_6]^{3+}$ is the more acidic of the two cations and has the lower pK_a value.

- Consider the compound $[CrCl(OH_2)_4(NCS)]Cl{\cdot}2H_2O$. **3**
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*.

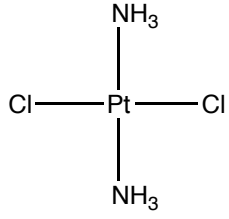
What is the oxidation state of the transition metal ion?	**+3 or (III)**
What is the coordination number of the transition metal ion?	**6**
How many *d*-electrons in the transition metal ion?	**Cr is in group 6 so Cr(III) is d^3**
List all the ligand donor atoms.	**Cl^-, 4 × O and N**

- 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. **3**

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.