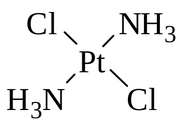
Marks
6

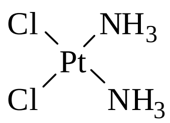
- Alfred Werner, one of the founders of the field of coordination chemistry, made extensive studies of the metal complex $[PtCl_2(NH_3)_2]$. He showed that it existed in two isomeric forms and used this information to predict that the compound had a square-planar molecular geometry. What other molecular geometry would need to be considered for such a complex and on what basis did Werner reject this alternative geometry?

As the complex contains 4 ligands bonded to Pt(II) (two Cl^- and two NH_3), a tetrahedral geometry also needs to be considered. However, as the angles between all of the bonds in a tetrahedron are the same, tetrahedral $[PtCl_2(NH_3)_2$ would not give rise to two isomers.

Draw and name the two isomers.



***trans*-diamminedichloridoplatinum(II)**



***cis*-diamminedichloridoplatinum(II)**

Why does platinum(II) form square-planar complexes?

There are a number of reasons why platinum(II) forms square-planar rather than tetrahedral complexes. These include:

(i) Pt(II) is a relatively big cation and so repulsion between the ligands are not too large.
(ii) The Pt-ligands bonds are stronger as, with its $5d^8$ configuration, Pt(II) is able to keep the d_{x2-y2} orbital completely empty allowing the ligands to donate into it.

Although the tetrahedral form has less crowding between the ligands, there is no single *d*-orbital which is directed towards, and can bond with, the ligands.

Which one of the isomers is biologically active? What is its activity? Describe two features of the complex that play important roles in this biological activity.

Only the *cis* isomer is biologically active - it is a potent anti-cancer drug.

The *cis* chloride ligands are easily replaced, allowing Pt(II) to bind to DNA and stop cell replication. It appears that the *cis*-geometry of the Pt-DNA bonds is important in this. The flat nature of the complex means it can approach the DNA closer.