

28.4 STEREOISOMERISM IN COMPLEXES

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🎯 Learning outcomes

Candidates should be able to:

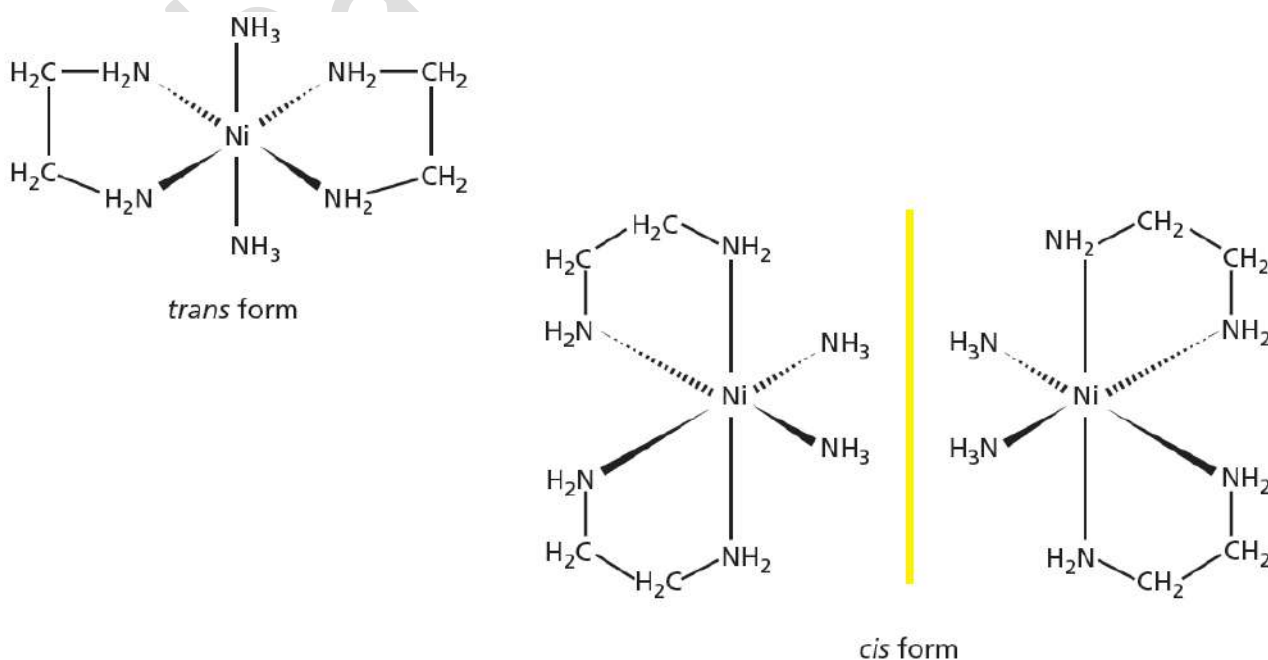
1. describe the types of stereoisomerism shown by complexes, including those associated with bidentate ligands:
 - (a) geometrical (*cis*/*trans*) isomerism, e.g. square planar such as $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and octahedral such as $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2(\text{H}_2\text{O})_2]^{2+}$
 - (b) optical isomerism, e.g. $[\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^{2+}$ and $[\text{Ni}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2(\text{H}_2\text{O})_2]^{2+}$
2. Deduce the overall polarity of complexes such as those described in 28.4.1(a) and 28.4.1(b)

Introduction

Some of the types of isomerism found in organic chemistry are also found in complex ions. An example of structural isomerism occurs in compounds of formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. Three such compounds are known with different properties. In particular, they have different numbers of free Cl^- ions (as shown by their reactions with Ag^+ ions) and free water molecules (as shown by the number of water molecules that are easily removed by dehydration).

Colour	Number of free Cl^- ions	Number of free H_2O molecules	Structure
purple	3	0	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+} 3\text{Cl}^-$
blue-green	2	1	$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+} 2\text{Cl}^- \cdot \text{H}_2\text{O}$
green	1	2	$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+ \text{Cl}^- \cdot 2\text{H}_2\text{O}$

Complexes can also show stereochemistry. A good example of this is the complex ion $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{2+}$, where 'en' is used as an abbreviation for 1,2-diaminoethane, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$. This complex can exist in *cis* and *trans* forms. The *cis* form (but not the *trans*) has a chiral centre (the cobalt atom) and can be resolved into optical isomers.



The overall polarity of the *trans* form is zero, since all the bond dipoles cancel. The *cis* form does have a dipole moment, however.

Geometric isomers

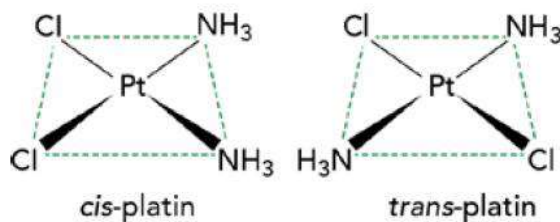
Molecules or ions with the same molecular formula and same bonds superimposed on each other, due to some lack of rotation around their bonds; these are also known as cis/trans isomers

The term 'geometric isomerism' refers to complexes with the same molecular formula but different geometrical arrangements of their atoms. Examples are any square planar complexes with the general formula $[M(A)_2(B)_2]$, where M is the transition element, and A and B are its surrounding ligands.

Cisplatin – a real-life application

An important example of *cis-trans* isomerism is the drug cisplatin. This has a Pt atom joined to two chlorine atoms and two ammonia molecules. It is a square planar complex and can, therefore, exist in both *cis* and *trans* forms.

In *cis*-platin, the chlorine atoms are next to each other in the square complex, but in *trans*-platin, they are diagonally opposite.



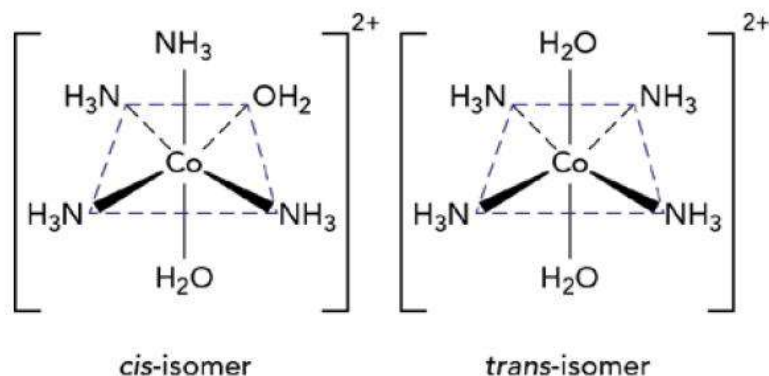
Cis-platin (but not *trans*-platin) is very effective in treating some forms of cancer. One of the chlorine atoms in *cis*-platin is easily hydrolysed to give the $[(NH_3)_2Cl(H_2O)]^+$ ion.

This ion binds to one of the four bases in DNA, usually guanine, to give the $[PtCl(\text{guanine-DNA})(NH_3)_2]^+$ ion. This ion can cross-link with another DNA chain by displacement of the chlorine from the complex. The cross-linking inhibits DNA replication, particularly in cancer cells that are undergoing rapid cell division, and the cell dies. There is no obvious reason why *trans*-platin is ineffective; one theory is that it becomes deactivated before it can attach itself to DNA.

- Differences in electronegativity of the atoms in ligands forming the dative bonds to the central transition metal ion can result in *polar and non-polar complexes*.
- For example, the *cis*-isomer will have two identical groups on one side of any square planar complex. So any difference in electronegativity between the two pairs of isomers will cause an imbalance of charge, making a *polar* complex.
- The atoms with the higher electronegativity have a stronger pull on the electrons in the dative bonds and will carry a partial negative charge.
- However, the *trans*-isomer will have identical ligands directly opposite each other at the corners of the square planar complex. So the pull on the electrons in the dative bonds to the central metal ion is perfectly balanced. This means that the charge is balanced and results in a *non-polar* complex.

Once again, the *trans* form has no dipole moment, whereas the *cis* form has one.

Octahedral complexes, with the general formula $[M(A)_4(B)_2]$, can also display geometric isomerism. An example is the cobalt(II) complex ion, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$



The *cis*-isomer is polar, whereas the *trans*-isomer is non-polar. The imbalance of charge in the *cis*-isomer results from the asymmetric shape of the *cis*- $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ isomer and the difference in electronegativity between the oxygen and nitrogen atoms bonded to the central cobalt(II).

The side of the complex with the water ligands will be partially negative, as oxygen is more electronegative than the nitrogen in the ammonia ligands. The differences in electronegativity still apply in the *trans*- $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ isomer, but its symmetrical arrangement ensures the charge in the complex is spread evenly around the complex.

cis- $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$

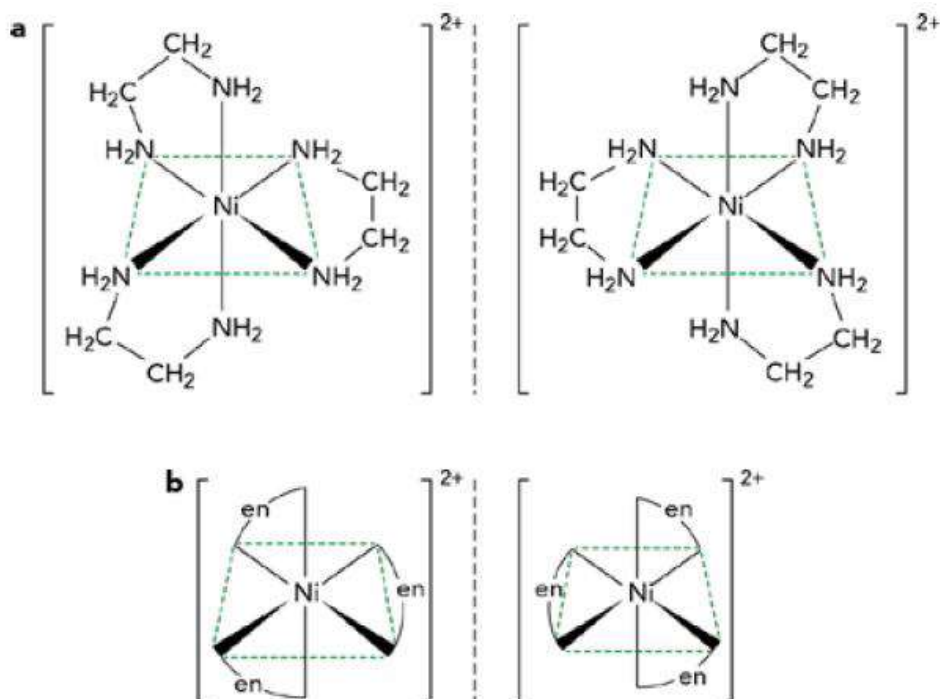
- the two H_2O ligands are on the same side
- the arrangement is asymmetric
- the bond dipoles do not cancel completely
- therefore, it is **polar**

trans- $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$

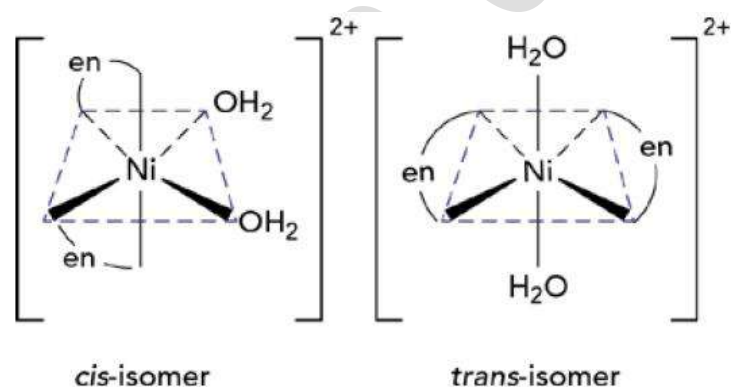
- the two H_2O ligands are opposite each other
- the arrangement is symmetrical
- bond dipoles cancel
- therefore, it is **non-polar**

Optical isomers are non-superimposable mirror images called enantiomers.

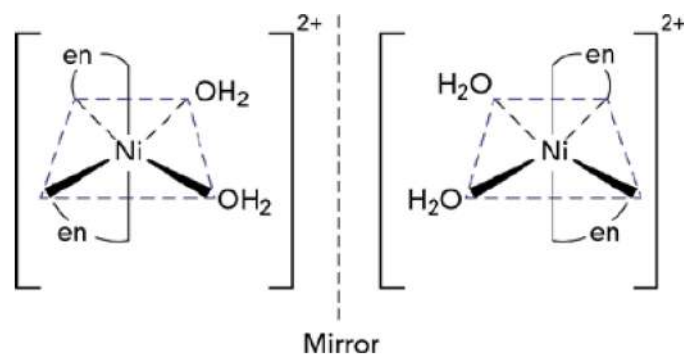
Stereoisomerism is also commonly shown by octahedral (six-coordinate) complexes associated with bidentate ligands. An example is the complex containing nickel as the transition metal and 1,2-diaminoethane ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) as the bidentate ligand. The two isomers are stereoisomers because the two different molecules are *mirror images* of each other and cannot be superimposed. They are optical isomers, differing only in their ability to rotate the plane of polarised light in opposite directions.



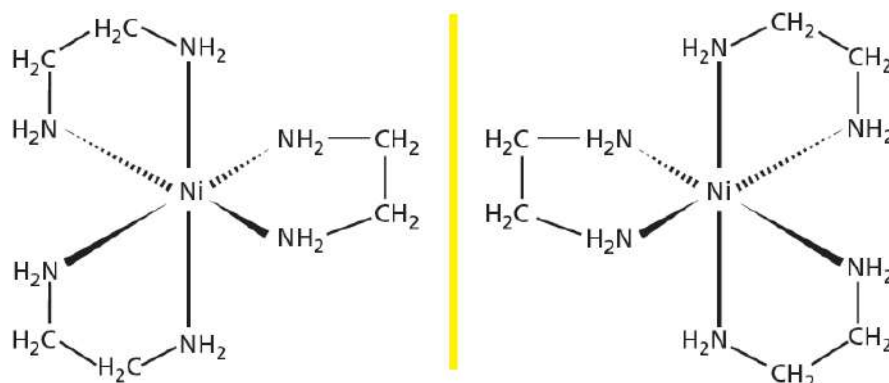
The complex ion consisting of nickel(II) bonded to two bidentate 1,2-diaminoethane (en) ligands and two monodentate ligands, such as water or chloride ions, can form both geometric (*cis/trans*) isomers and optical isomers. Look at the *cis*- and *trans*-isomers of $[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2(\text{H}_2\text{O})_2]^{2+}$ in Figure 24.11, simplified to $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$.



Of the two *cis*- and *trans*- isomers of $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$, only the *cis*- isomer is optically active, with its two non-superimposable mirror images. The symmetrical nature of the *trans*-isomers of $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ means that its mirror images can be superimposed, so they do not display optical isomerism. Look at the optical isomers of $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ in Figure



Ni^{2+} forms a complex with three 1,2-diaminoethane ligands. This has only the *cis* form, as the distance is too large for the ligand to stretch across the *trans* positions. The *cis* form can also be resolved into optical isomers



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