Isomerism in Coordination Compounds

Lecture 6. CHEM1902 (C 10K) Coordination Chemistry

Two or more different compounds having the same formula are called isomers. Two principal types of isomerism are known among coordination compounds. Each of which can be further subdivided.

1. Stereoisomerism.
a) Geometrical isomerism
b) Optical isomerism
2. Structural Isomerism.
a) Coordination isomerism
b) Ionisation isomerism
c) Hydrate isomerism
d) Linkage isomerism

1. Stereoisomers

Stereoisomers have the same atoms, same sets of bonds, but differ in the relative orientation of these bonds.

Ignoring special cases involving esoteric ligands, then:
Geometric isomers are possible for both square planar and octahedral complexes, but not tetrahedral.

Optical isomers are possible for both tetrahedral and octahedral complexes, but not square planar.

The earliest examples of stereoisomerism involve complexes of Co^{3+}. In 1889, Jorgensen observed purple and green salts of $[Co(en)_2Cl_2]+$, which Werner later correctly identified as the *cis*- and *trans*- geometric isomers. In 1911, the first resolution of optical isomers was reported by Werner and King for the complexes cis-$[CoNH_3(en)_2X]^{2+}$, where X=Cl- or Br-.

Geometric Isomers

The number of geometric isomers expected for common stereochemistries are as follows:

Square Planar:

Compound type	No. of isomers
Ma_2b_2	2 (cis- and trans-)
Mabcd	3 (use cis- and trans- relations)

here a, b, c, and d refer to monodentate ligands (see Figures 8 and 9 of the Handout which are reproduced below).

A number of examples of these types have been isolated and characterised and they show very different chemical and biological properties. Thus for example, *cis*-$Pt(NH_3)_2Cl_2$ is an anti-cancer agent (cisplatin) whereas the *trans*- isomer is inactive against cancer (it is toxic), and so not useful in Chemotherapy.

Figure 8. *cis*- and *trans*- isomers of $[Pt(NH_3)_2Cl_2]$

cis- and *trans*- refer to the position of 2 groups relative to each other. In the *cis*- isomer they are "next to each other" i.e. at 90 degrees in relation to the central metal ion, whereas in the *trans*- isomer they are "opposite each other", i.e. at 180 degrees relative to the central metal ion.

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a
|
|
M ----b         a----M----b
  cis-            trans-
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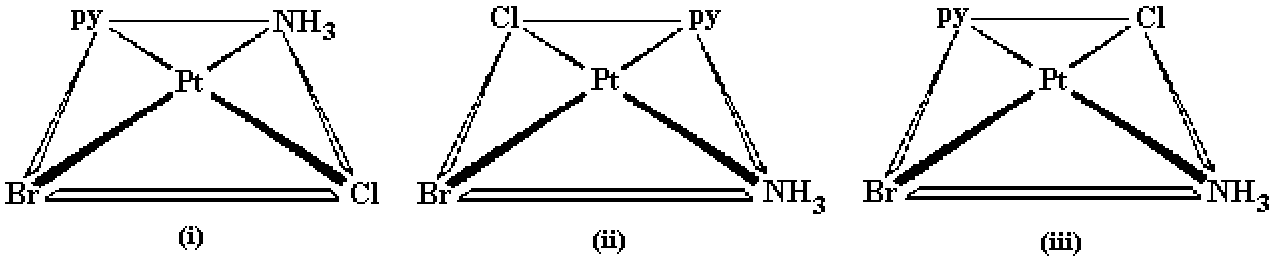


Figure 9. 3 geometric isomers of a square planar complex [$PtNH_3BrClpy$].

The first report of the three geometric isomers being isolated and characterised for complexes of the type [Mabcd] was by Il'ya Chernyaev in 1928. The example above was reported by Anna Gel'man in 1948.

Question. Does *cis*-amminebromo-*cis*-chloropyridineplatinum(II) uniquely identify isomer 9(ii)??

Octahedral:

Compound type	No. of isomers
Ma_4b_2	2 (cis- and trans-)
Ma_3b_3	2 (fac- and mer-)
MAA_2b_2	3 (2*cis- and 1 trans-)

here a, and b, are monodentate ligands and AA is a bidentate ligand (see Figures 10, 11, 12 in the Handout).

In the second example, new labels are introduced to reflect the relative positions of the ligands around the octahedral structure. Thus; placing the 3 groups on one face of the ocathedral gives rise to the *fac*ial isomer and placing the 3 groups around the centre gives rise to the *mer*idinal isomer.

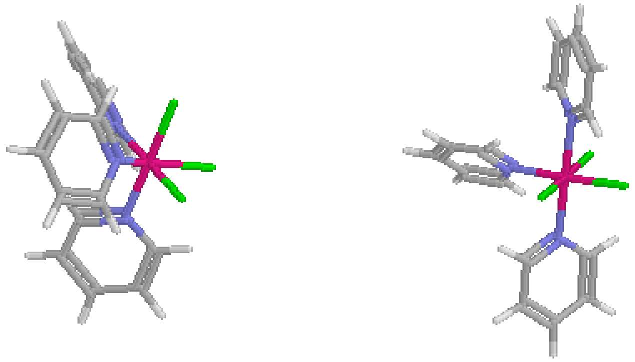


Figure 11. *fac*- and *mer*- isomers of [Rhpy$_3$Cl$_3$].

[Mabcdef] is expected to give 15 geometric isomers. In the case of [Pt(NH$_3$)BrClIpyNO$_2$], several of these were isolated and characterised by Anna Gel'man and reported in 1956. Optical isomers are possible for each of these 15 forms, making a total of 30 isomers.

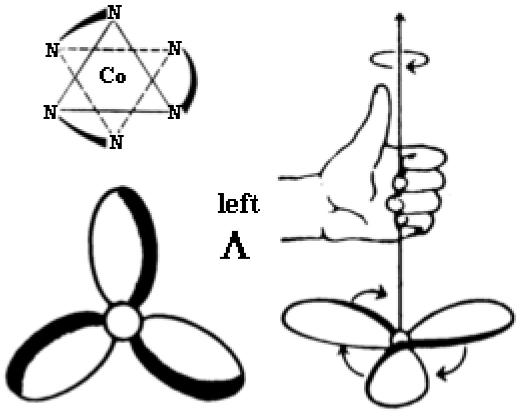
The *cis*- isomer of MAA$_2$b$_2$ may also exhibit optical isomerism (see Figure 12) although we will concentrate largely on optical isomers of the type M(AA)$_3$ (see below).

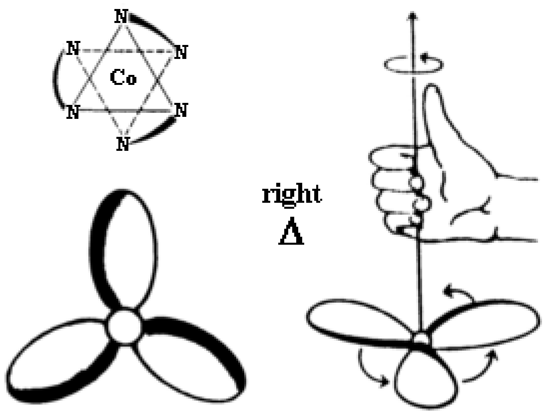
Optical Isomers

Optical isomers are related as non-superimposable mirror images and differ in the direction with which they rotate plane-polarised light. These isomers are referred to as enantiomers or enantiomorphs of each other and their non-superimposable structures are described as being asymmetric.

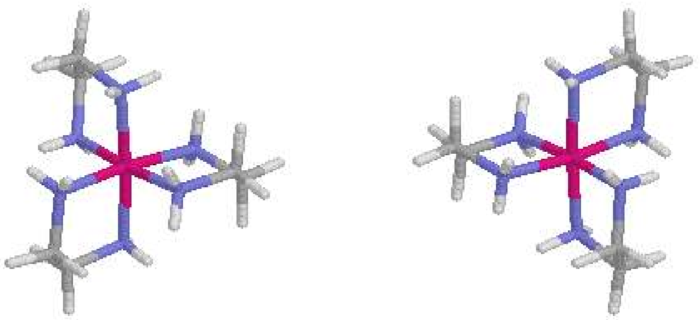
Various methods have been used to denote the absolute configuration of optical isomers such as D or L, R or S and Λ or Δ. The 1970 IUPAC rules suggest that helixes are defined and then designated Lambda Λ (left- D) and Delta Δ (right-L) in much the same way as we would look at three-bladed propellors and determine whether they would trace out a left or right handed helix.

Figure 12. The absolute configuration of [Co(en)$_3$]$^{3+}$





The two isomers have identical chemical properties and just denoting their absolute configuration does NOT give any information regarding the direction in which they rotate plane-polarised light. This can ONLY be determined from measurement and then the isomers are further distinguished by using the prefixes laevo ((-) or l) and dextro ((+) or d) depending on whether they rotate left or right. The use of l- and d- is not recommended since it may appear to conflict with L and D.



To add to the confusion, when measured at the sodium D line (589nm), the tris(1,2-diaminoethane)M(III) complexes (M= Rh(III) and Co(III)) with **IDENTICAL** absolute configuration, rotate plane polarised light in **OPPOSITE** directions! The Λ (D)-$[Co(en)_3]^{3+}$ isomer gives a rotation to the right and therefore corresponds to the (+) isomer.

Since the successful resolution of an entirely inorganic ion (containing no C atoms) (hexol) only a handful of truly inorganic complexes have been isolated as their optical isomers eg $(NH_4)_2\ Pt(S_5)_3.2H_2O$.

Note that, although it is predicted that tetrahedral complexes with 4 different ligands should be able to give rise to optical isomers (compare C chemistry), in general they are too labile and can not be isolated.

2. Structural Isomers

There are several types of this isomerism frequently encountered in coordination chemistry and the following represents some of them.

- a) Coordination isomerism: where compounds containing complex anionic and cationic parts can be thought of as occurring by interchange of some ligands from the cationic part to the anionic part.

one isomer	$[Co(NH_3)_6]\ [Cr(C_2O_4)_3]$
another isomer	$[Co(C_2O_4)_3]\ [Cr(NH_3)_6]$

- b) Ionisation isomers: where the isomers can be thought of as occurring because of the formation of different ions in solution.

one isomer	$[Pt(NH_3)_3Br]NO_2$ -> NO_2- anions in solution
another isomer	$[Pt(NH_3)_3NO_2]Br$ -> Br- anions in solution

Notice that both anions are necessary to balance the charge of the complex, and that they differ in that one ion is directly attached to the central metal but the other is not. A very similar type of isomerism results from replacement of a coordinated group by a solvent molecule (Solvate Isomerism). In the case of water, this is called Hydrate isomerism.

- c) Hydrate isomerism: the best known example of this occurs for chromium chloride "$CrCl_3.6H_2O$" which may contain 4, 5, or 6 coordinated water molecules.

$[Cr(H_2O)_4Cl_2]Cl.2H_2O$ bright-green
$[Cr(H_2O)_5Cl]Cl_2.H_2O$ grey-green
$[Cr(H_2O)_6]Cl_3$ violet

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test for Cl- ions, would find 1, 2, and 3 Cl- ions in solution respectively.

- d) Linkage isomerism occurs with ambidentate ligands. These ligands are capable of coordinating in more than one way. The best known cases involve the monodentate ligands SCN- / NCS- and NO_2^- / ONO^-.

For example:

$[Co(NH_3)_5ONO]Cl$ the nitrito isomer -O attached
$[Co(NH_3)_5NO_2]Cl$ the nitro isomer - N attached.

Inorganic Nomenclature

As part of this course, you are required to make yourselves familiar with the rules related to Inorganic Nomenclature.

Uses of Coordination Compounds

A brief survey of some of the uses of coordination compounds includes:

l. Dyes and Pigments: Coordination compounds have been used from the earliest times as dyes and pigments, for example madder dye which is red, was used by the ancient Greeks and others. It is a complex of Hydroxyanthraquinone. A more modern example is the pigment copper phthalocyanine, which is blue.

2. Analytical Chemistry: You have already encountered many such uses during the laboratory course.

(a) Colour Tests: Since many complexes are highly coloured they can be used as colourimetric reagents e.g. formation of red 2,2'-bipyridyl and l,l0-phenanthroline complexes as a test for Fe^{2+}

(b) Gravimetric Analysis: Here chelating ligands are often used to form insoluble complexes e.g. $Ni(DMG)_2$ and $Al(oxine)_3$ (see laboratory manual).

(c) Complexometric Titrations and Masking Agents: An example of this is the use of EDTA in the volumetric determination of a wide variety of metal ions in solution, e.g. Zn^{2+}, Pb^{2+}, Ca^{2+},Co^{2+}, Ni^{2+}, Cu^{2+}, etc. By careful adjustment of the pH and using suitable indicators, mixtures of metals can be analysed, e.g. Bi^{3+} in the presence of Pb^{2+} (see laboratory manual). Alternatively, EDTA may be used as a masking agent to remove a metal ion which would interfere with the analysis of a second metal ion present.

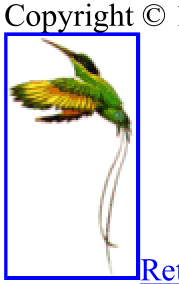
3. Sequestering Agents: Related to their use as masking agents is the use of ligands for "sequestering" i.e. for the effective removal of objectionable ions from solution in industrial processing, e.g. EDTA is used to "soften" water. The addition of EDTA to water is used in boilers etc., to prevent "scaling" or build up of insoluble calcium salts.

4. Extraction of Metals: Sometimes certain metals can be leached from their ores by formation of stable complexes e.g. Ag and Au as complexes of cyanide ion.

5. Bio-Inorganic Chemistry: Naturally occurring complexes include haemoglobin, chlorophyll, vitamin B12 etc. EDTA and other complexing agents have been used to speed the elimination of harmful radioactive and other toxic elements from the body. (e.g. Pb^{2+}). In these cases a soluble metal chelate is formed.

6. Chemo-therapy: an example here is the use of cis-$Pt(NH_3)_2Cl_2$ as an anti-tumour drug.

Return to Coordination Chemistry course outline.



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