Chem Factsheet

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Isomerism In Transition Metal Complexes

Isomerism is usually associated with organic molecules but the concept also applies to some transition metal complexes.

SOME RELEVANT DEFINITIONS

1. ISOMERS

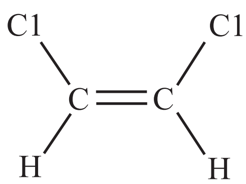
Particles having the same molecular formula but different structures.
e.g. Ethanol (CH_3CH_2OH) and methoxymethane (CH_3OCH_3) both have moleculatr formula C_2H_6O.

2. STRUCTURAL ISOMERS

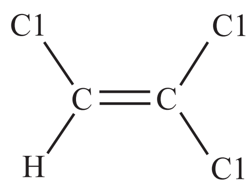
Isomers which have different bonding patterns between their constituent atoms.
e.g. 1-chloropropane ($CH_3CH_2CH_2Cl$) and 2-chloropropane ($CH_3CHClCH_3$)

3. STEREOISOMERS

Isomers with the same bonding patterns between their constituent atoms but different arrangements of atoms / groups in 3D space.
e.g.



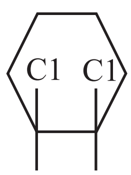
cis-1,2-dichloroethene



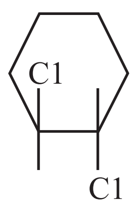
trans-1,2-dichloroethene

4. GEOMETRIC ISOMERS

Stereoisomers resulting from the different positioning of groups about a non-rotatable double bond or ring structure.
e.g.1 cis and trans-1,2-dichloroethene (see above) – also called Z and E isomers.
e.g. 2



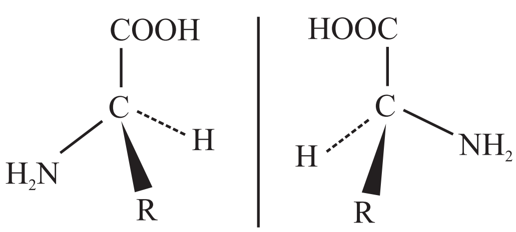
cis-1,2-dichlorocyclohexane



trans-1,2-dichlorocyclohexane

5. OPTICAL ISOMERS (or ENANTIOMERS)

Stereoisomers which are non-superimposable mirror images of each other. Alpha amino acids are a common example.
e.g.



6. TRANSITION METAL COMPLEX

A particle formed from a central transition metal ion (or atom) with a fixed number of molecules or negative ions (called ligands) bonded to it by coordinate (dative) bonds.
e.g. $[CuCl_4]^{2-}$, $[Co(NH_3)_6]^{3+}$, $[Cr(NH_2CH_2CH_2NH_2)_3]^{3+}$.

7. LIGAND

A molecule or negative ion with available lone pairs which it can share with the incomplete d-subshell of a transition metal ion (atom) to form a coordinate (dative) bond.

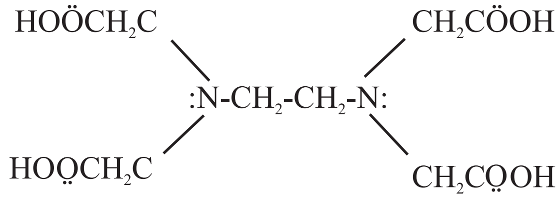
8. DENTICITY OF A LIGAND (D)

The number of coordinate bonds from a ligand to the central transition metal ion (atom) in a complex.
e.g. $:Cl^-$, $:NH_3$ have denticity 1 (monodentate ligands) whereas $NH_2CH_2CH_2NH_2$ has denticity 2 (bidentate ligand) because there is one lone pair on each N atom.

> **Note:** The chloride ion has 4 lone pairs but only one is available for bonding. The others are "pointing in the wrong direction" to also bond.

The "spacing" by 2 C atoms between the N atoms in 1,2-diaminoethane allows sufficient flexibility of the ligand for both lone pairs to form bonds.
Ligands such as EDTA (ethylene diammine tetraacetic acid) are said to be hexadentate (or sometimes just multidentate) because each particle, because of its flexibility [again, each lone pair bearing atom spaced by 2 C atoms], can form 6 bonds to the same central transition metal ion (atom) in a complex.

EDTA



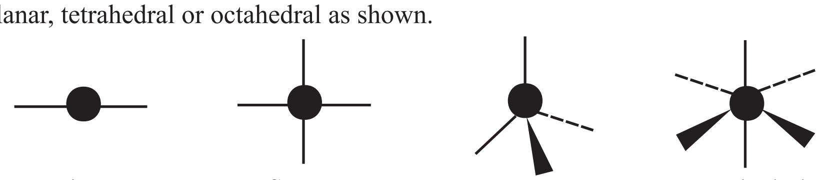
9. COORDINATION NUMBER (CN) OF A TRANSITION METAL ION (ATOM)

The number of coordinate bonds formed from the various ligands to the transition metal ion (atom) in a complex.
e.g. 2, 4 and 6 are the common coordination numbers.

> **Note:** The number of ligands per central transition metal ion (atom) is given by CN/D.

10. COORINATION GEOMETRY

The shape created by the distribution of the coordinate bonds around the central transition metal ion (atom) [●] in a complex. These are usually linear, square planar, tetrahedral or octahedral as shown.



Linear | Square planar | Tetrahedral | Octahedral

APPLYING THESE IDEAS TO TRANSITIONMETAL COMPLEXES

> **Note:** This FactSheet will **not** deal with the possibility of isomerism occurring within a ligand.

e.g. 1-aminopropane [$CH_3CH_2CH_2NH_2$] and 2-aminopropane [$CH_3CH(NH_2)CH_3$].
Here we are concerned with isomerism created by variations in ligands, ligand numbers and coordination geometry.

A. LINEAR COMPLEXES

As shown in the general and specific examples, linear complexes **do not show isomerism** because the particle is symmetrical for any combination of monodentate ligands (L) and transition metal ion (M).

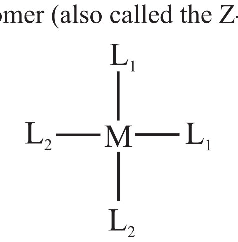
$[L_1 — M — L_2]^{n+/-}$ A general linear complex

$[{}_3HN — Ag — NH_3]^{+}$ Diammine silver(I)ion

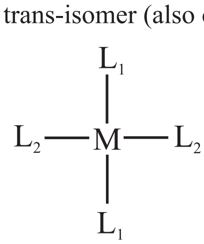
$[C1 — Cu — C1]^{-}$ Dichloro copper(I) ion

B. SQUARE PLANAR COMPLEXES

When two different monodentate ligands (L1 and L2) are involved, **cis-trans isomerism can occur**. Similar ligands are either at 90° to each other in the cis-isomer (also called the Z-isomer) or at 180° to each other in the trans-isomer (also called the E-isomer).



General cis (or Z) isomer

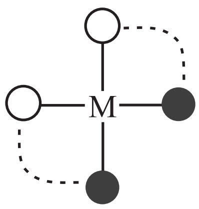


General trans (or E) isomer

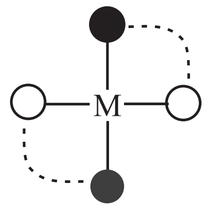
Q1 Draw the structures of the isomers of "platin" (diamminedichloroplatinum(II)), $[Pt(NH_3)_2Cl_2]$. Identify which is cis and which is trans.

> **Note:** The cis isomer of platin (see q1) is a common anti-cancer drug. Its shape allows it to bind to cancer cell DNA, eventually killing the cell. In contrast, trans-platin is not pharmacologically active because of its different shape. In fact, it is toxic, and it is essential to test batches of cis-platin for the absence of the trans isomer!

cis-trans is also possible with *asymmetric* bidentate ligands (●-------○) where ● and ○ represent two different groups, both with lone pairs that can form coordinate bonds and "-------" represents a two carbon chain.



General cis (or Z) isomer

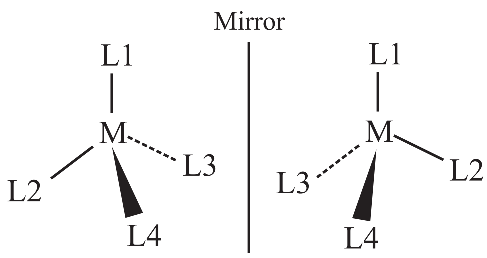


General trans (or E) isomer

Q2 Draw the structure of the *trans* isomer of $[Au(HOCH_2CH_2NH_2)_2]$.

C. TETRAHEDRAL COMPLEXES

As in organic molecules, optical isomers (enantiomers) of transition metals complexes can occur if four *different* monodentate ligands (L1-L4) are bonded to the transition metal. One isomer is the non-superimposable mirror image of the other (i.e. they are *chiral*) and they rotate the plane of plane-polarised light equally but in opposite directions.



Q3 Draw the structure of the optical isomers of $[Cr(CN)(NH_3)(Cl)(H_2O)]^+$.

> **Note:** rather than copying one isomer in an "imaginary" mirror to get the other isomer, merely swap the position of any two ligands.

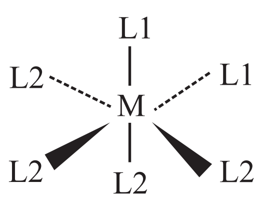
D. OCTAHEDRAL COMPLEXES

Both geometric (cis-trans) and optical isomers can occur in octahedral complexes.

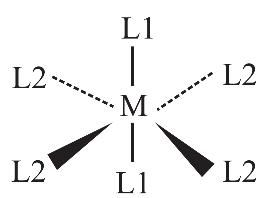
(1) GEOMETRIC ISOMERS

This occurs for complexes with either of the two following general structures

(a) $M(L1)_2(L2)_4$ where L1 and L2 are monodentate ligands



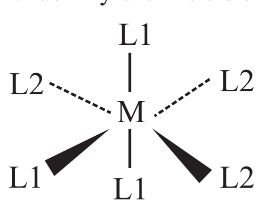
General *cis* isomer



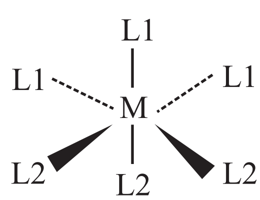
General *trans* isomer

Q4 Draw the geometric isomers of $[Co(NH_3)_4Cl_2]^+$. Identify each as cis or trans.

(b) $M(L1)_3(L2)_3$ where L1 and L2 are monodentate ligands



General *mer* isomer

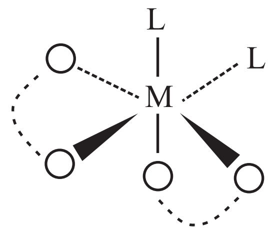


General *fac* isomer

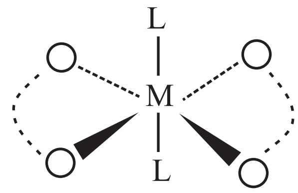
> **Note:** *mer* stands for meridional – any 3 similar ligands lie in the same plane.
> *fac* stands for facial – any 3 similar ligands are all at 90°to each other.

Q5 Draw the geometric isomers of $[Co(NH_3)_3Cl_3]$. Identify each as mer or fac.

(c) $M(L)_2(B)_2$ where L is a monodentate ligand and B a bidentate ligand (○-----○)



General *cis* isomer



General *trans* isomer

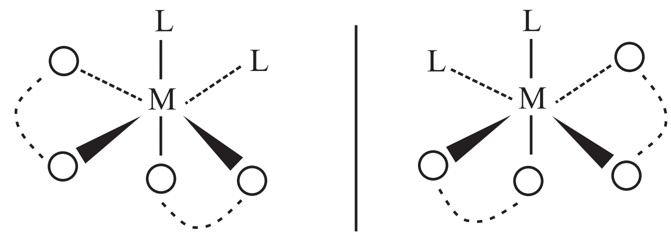
Note: The cis isomer can also exist as optical isomers – see below.

(2) OPTICAL ISOMERS

This occurs for complexes with either of the two following general structures

(a) $M(L)_2(B)_2$ where L is a monodentate ligand and B a bidentate ligand (○-----○)

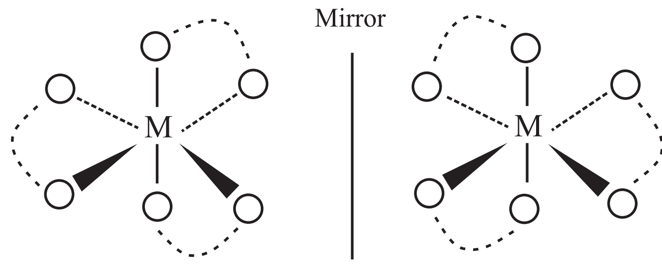
Mirror



Note: These are optically active isomers of the cis isomer of) $M(L)_2(B)_2$

((b) $M(B)_3$ where B is a bidentate ligand (○-----○)

Mirror



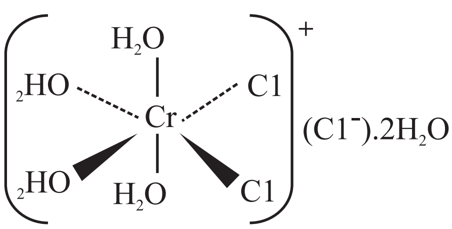
Q6 Draw the geometric and optical isomers of $[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$

Q7 Draw the optical isomers of $[Cu(C_2O_4)_3]^{4-.}$

E. HYDRATE ISOMERS

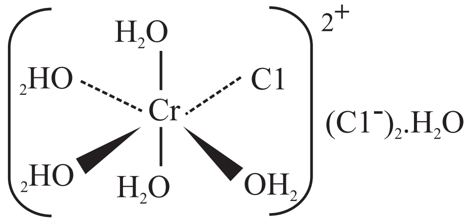
In general, this is a type of *structura*l isomerism rather than geometric or optical.
The best known example of this occurs for chromium chloride "$CrCl_3.6H_2O$" which occurs in three distinct crystalline forms because it can contain 4, 5, or 6 water molecules coordinated to the chromium(III) ion along with 2, 1 or 0 chloride ligands respectively. The remaining chloride ions and water molecules are counterions or waters of crystallization respectively.

$[CrCl_2(H_2O)_4]Cl.2H_2O$



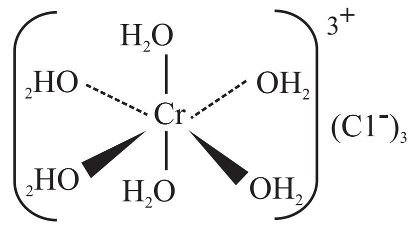
Bright-green crystals

$[CrCl(H_2O)_5]Cl_2.H_2O$



Grey-green crystals

$[Cr(H_2O)_6]Cl_3$

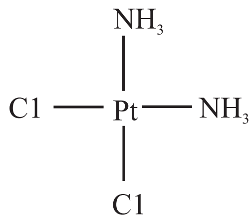


Violet crystals

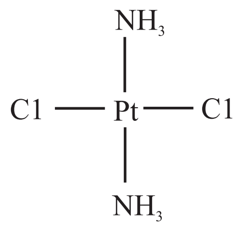
Q8 Which of the above complexes can also show geometric isomerism?

ANSWERS TO QUESTIONS

Q1

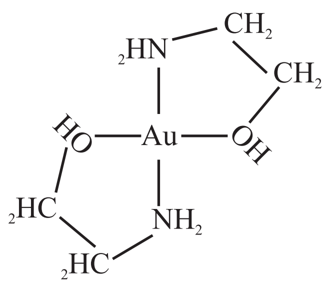


cis-platin

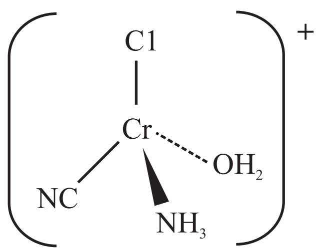


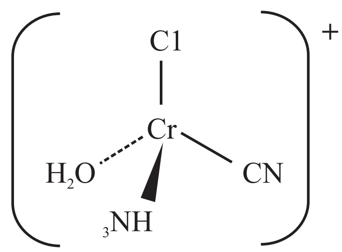
trans-platin

Q2

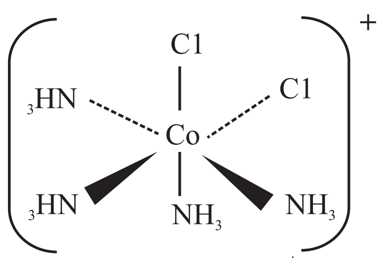


Q3

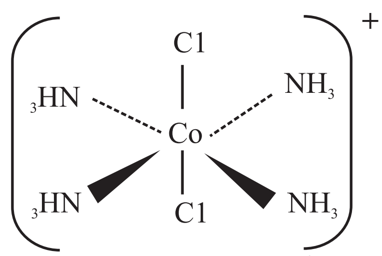




Q4

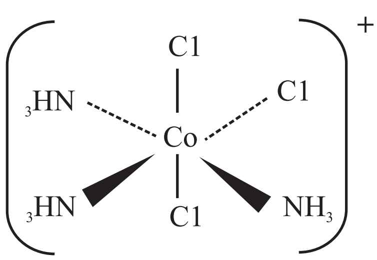


cis $[Co(NH_3)_4Cl_2]^+$

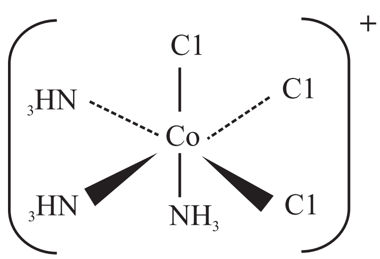


trans $[Co(NH_3)_4Cl_2]^+$

Q5



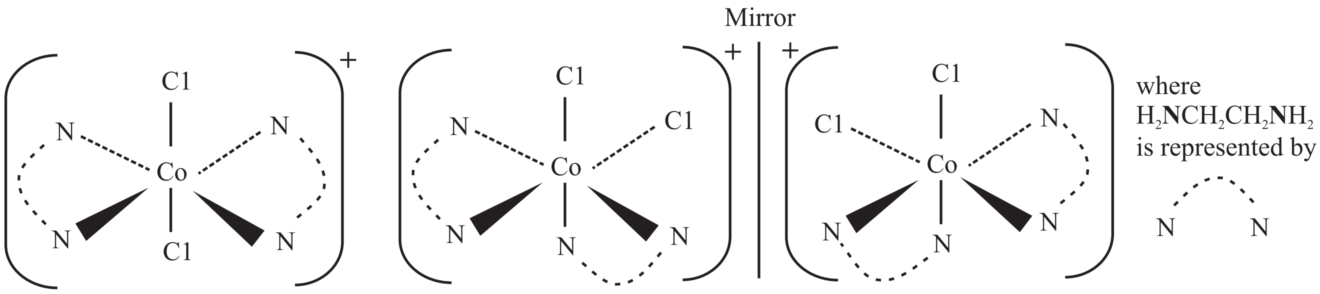
mer $[Co(NH_3)_3Cl_3]$



fac $[Co(NH_3)_3Cl_3]$

ANSWERS TO QUESTIONS

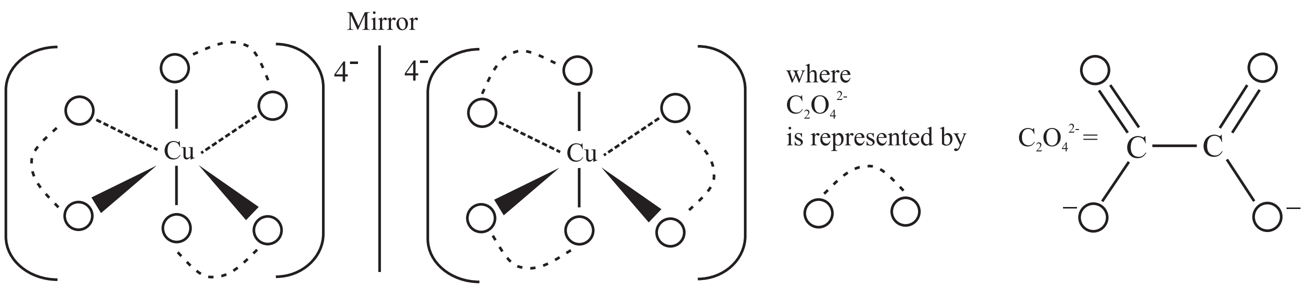
Q6



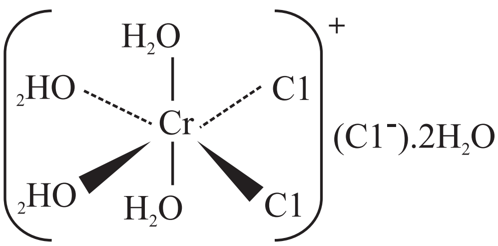
trans isomer

Optical isomers of the *cis* isomer

Q7



Q8



This is the cis isomer. The trans isomer is given if the 2 chloro ligands are at 180° to each other.

Acknowledgements: *This Factsheet was researched and written by Mike Hughes.*
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