



CHEMISTRY

15th class Date : 01-10-2021

Dr. K. Ananthanarayanan
Associate Professor (Research)
Department of Chemistry
Room No 319, 3rd Floor, Raman Research Park

Email : ananthak@srmist.edu.in

Phone : +91-9840154665



Last class...

- ☐ CFT – problem solving

Last class...



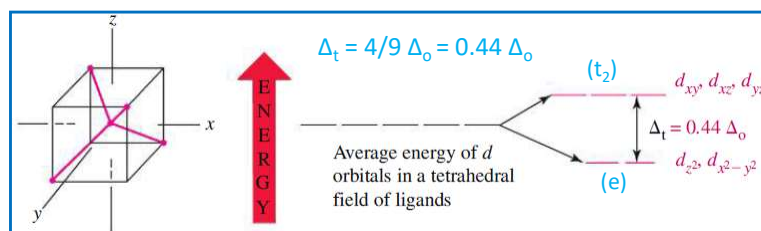
- ☐ Crystal Field Theory – problem solving
- ☐ Isomerism in coordination complexes, Introduction

In this class...



- ☐ Isomerism in coordination complexes, continuation

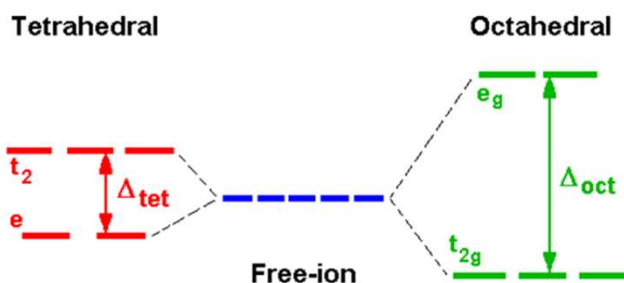
Crystal Field Theory: Summary, Tetrahedral Complexes



- Imagine a tetrahedral molecule inside a cube with **metal ions in the center** of the cube. The **ligands occupy the four alternate corners of the cube** leaving the rest four corners empty.
- The **two 'e' ($d_{x^2-y^2}$ and d_{z^2}) orbitals point to the center of the face of the cube** while the **three 't₂' (d_{xy} , d_{yz} and d_{zx}) orbitals point to the center of the edges of the cube.**
- Thus, the **t₂ orbitals are nearer to the direction of approach of the ligands** than the e orbitals. **(The ligands do not directly approach any of the metal d orbitals)**

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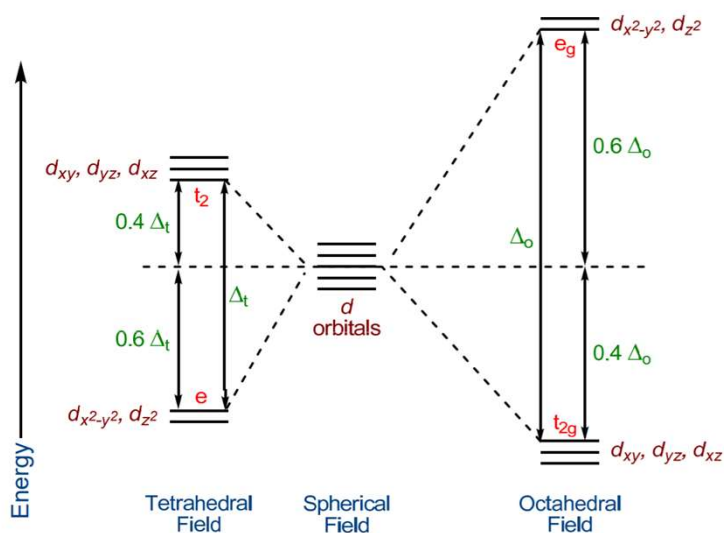
- The energy of t₂ orbitals is raised 0.4 Δ_t while the energy of e orbitals is lowered 0.6 Δ_t
- **In case of tetrahedral complex, since $\Delta_t < P$, the electrons tend to remain unpaired and hence only high spin tetrahedral complexes are known.**

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Crystal Field Theory: summary



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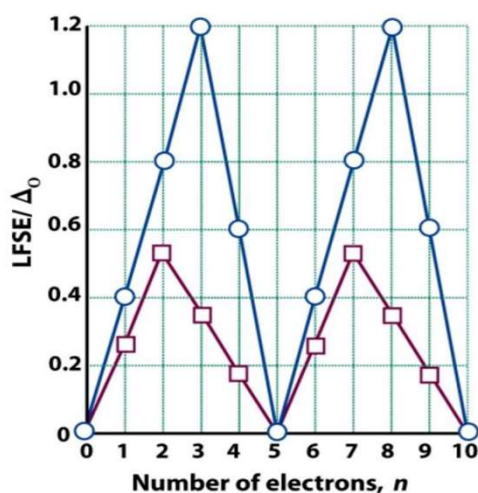
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Crystal Field Theory: summary



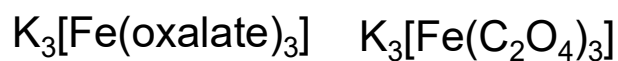
Octahedral vs Tetrahedral Field



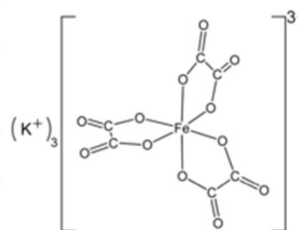
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	$\text{K}_3[\text{Fe}(\text{oxalate})_3] \cdot 3\text{H}_2\text{O}$
metal ion	Fe^{3+}
number of d electrons	$5 - t_{2g}^3 e_g^2$
stereochemistry	octahedral
High Spin/Low Spin	High Spin
# of unpaired electrons	5
magnetic moment	$\sqrt{35}$ B.M

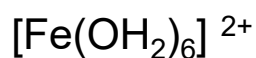


	$\text{K}_2[\text{CuCl}_4]$
metal ion	Cu^{2+}
number of d electrons	$9 - e^4 t_2^5$
stereochemistry	tetrahedral
High Spin/Low Spin	Not relevant (all High spin)
# of unpaired electrons	1
magnetic moment	$\sqrt{3}$ B.M



Predict the configuration, the number of unpaired electrons, ligand field stabilization energy and account for which are likely to be strong-field and weak-field. Comment on the magnetic property also.

- (a) $[\text{Fe}(\text{OH}_2)_6]^{2+}$
- (b) $[\text{Fe}(\text{CN})_6]^{3-}$
- (c) $[\text{FeCl}_4]^{2-}$



- ☐ The iron ion in this octahedral complex with six neutral water ligands is in the 2+ oxidation state, and water is low on the spectrochemical series.
- ☐ We certainly expect this d^6 ion to be in a high spin configuration, $t_{2g}^4 e_g^2$.
- ☐ That is, it has four unpaired electrons and is strongly paramagnetic.
- ☐ The LFSE is $4 \times -0.4\Delta_o + 2 \times 0.6\Delta_o = -0.4\Delta_o$.



- ❑ The iron in this octahedral complex with six cyanide ligands is in the 3+ oxidation state, and cyanide is high on the spectrochemical series.
- ❑ This is almost certainly a complex with a low spin configuration.
- ❑ Fe^{3+} is a d5 metal ion, and hence the configuration will be $t_{2g}^5 e_g^0$
- ❑ The LFSE is $5 \times -0.4\Delta_o = -2.0\Delta_o$.
- ❑ It has one unpaired electron and is weakly paramagnetic.



- ❑ This is a tetrahedral complex, because the ligands are -1 , the metal is therefore $2+$, and Fe^{2+} is d^6 , which is not a candidate for square planar geometry.
- ❑ Remember that all tetrahedral complexes are high spin because ΔT is inherently small $\{\Delta T = (4/9)\Delta_o\}$.
- ❑ Thus the expected electron configuration is $e^3 t_2^3$, for four unpaired electrons, and strongly paramagnetic.
- ❑ The LFSE is $3 \times -0.6\Delta T + 3 \times 0.4\Delta T = -0.6\Delta T$.



Which of the following complex will have a magnetic moment of 1.73 BM and calculate the unpaired electrons in each of the complex?

- A. TiCl_4
- B. $[\text{CoCl}_6]^{4-}$
- C. $[\text{Cu}(\text{NH}_3)_4]^{2+}$
- D. $[\text{Ni}(\text{CN})_4]^{2-}$

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Electronic configuration of Cu^{2+} ion in $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

Cu^{2+} ion = $[\text{Ar}]3d^94s^0$.

$\therefore \text{Cu}^{2+}$ ion has one unpaired electron.

Magnetic moment of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ (μ) = $\sqrt{n(n+2)}$ BM

where, n = no. of unpaired electrons

$$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73\text{BM}$$

Nickel complex - 2 unpaired electrons

Titanium complex - 0 unpaired electrons

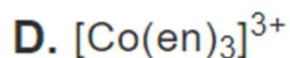
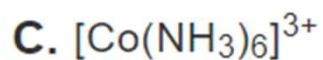
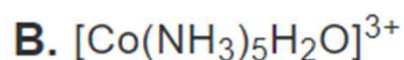
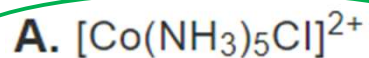
Cobalt complex - 3 unpaired electrons

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The wavelength of light absorbed is highest in ?



The crystal field stabilisation energy (CFSE) is highest for ?



Higher the oxidation state of the metal, greater the crystal field splitting. In options (a), (b) and (d), Co is present in +2 oxidation state and in (c) it is present in +3 oxidation state and hence, $[\text{Co}(\text{NH}_3)_6]^{3+}$ has a higher value of CFSE.

[Fe(H₂O)₆]³⁺ ion is practically colourless but its solution becomes red when NCS⁻ ions are added to it. Why ?

- ❑ [Fe(NCS)₆]³⁻ is formed by adding NCS⁻ into [Fe(H₂O)₆]³⁺.
- ❑ Since H₂O is a weak ligand, [Fe(H₂O)₆]³⁺ has so small value of Δ_o that the wavelength of the absorption peak of this ion lies in the IR region and hence this ion appears colourless.
- ❑ Now NCS⁻ is a strong ligand, the presence of these ligands in [Fe(NCS)₆]³⁻ makes the value of Δ_o high so that the wavelength of the absorption peak lies in the visible region.

Calculate the octahedral crystal field splitting energy in kJ/mol for [Fe(CN)₆]⁴⁻, if the wavelength of the most intensely absorbed light is 305 nm.

$$\Delta_o = h\nu \quad \nu = c/\lambda \quad \Delta_o = hc/\lambda$$

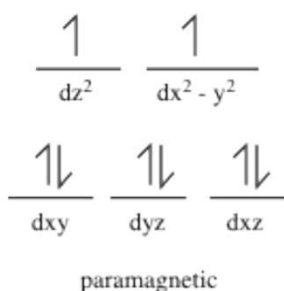
$$\Delta_o = 6.6261 \times 10^{-34} \text{ Js } \frac{(2.9979 \times 10^8 \text{ m/s})}{305 \times 10^{-9} \text{ m}}$$

$$\Delta_o = 6.513 \times 10^{-19} \text{ J}$$

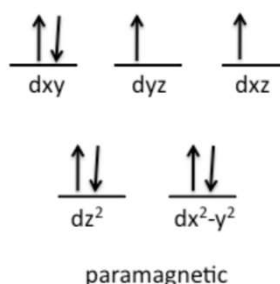
$$6.513 \times 10^{-19} \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times 6.02214 \times 10^{23} \frac{\text{molecules}}{\text{mol}} = 392 \text{ kJ/mol}$$

Comment on the magnetic behaviour of Ni^{2+} coordination complex. Draw the crystal field splitting diagrams for an octahedral crystal field and a tetrahedral crystal field, labeling the d-orbitals and explain.

OCTAHEDRAL DIAGRAM



TETRAHEDRAL DIAGRAM



For each of the following pairs of complexes, indicate the one that has the larger LFSE (more stabilization):

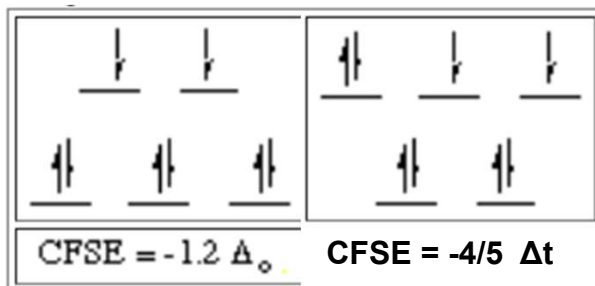
(a) $[\text{Cr}(\text{OH}_2)_6]^{2+}$ or $[\text{Mn}(\text{OH}_2)_6]^{2+}$

(b) $[\text{Mn}(\text{OH}_2)_6]^{2+}$ or $[\text{Fe}(\text{OH}_2)_6]^{3+}$

a) Both complexes have the same ligands, water, which is a weak ligand, so the LFSE is determined by the electron configuration. Cr^{2+} is d^4 , or $t_{2g}^3 e_g^1$ with $\text{LFSE} = -6Dq$ while Mn^{2+} is d^5 , or $t_{2g}^3 e_g^2$ with $\text{LFSE} = 0$. **$[\text{Cr}(\text{OH}_2)_6]^{2+}$ has the larger LFSE (more stabilization).**

b) Both complexes have the same ligands, water, which is a weak ligand, and both are d^5 or $t_{2g}^3 e_g^2$ so the **$\text{LFSE} = 0$ for both complexes.**

The complex ion $[\text{NiCl}_6]^{4-}$ has an octahedral splitting energy of 81 kJ/mol. Calculate its CFSE in kJ/mol. Assume that the tetrahedral splitting energy is equal to 4/9 of the octahedral splitting energy, and calculate the CFSE of $[\text{NiCl}_4]^{2-}$ in kJ/mol.



□ Octahedral CFSE = $-1.2 \times 81 \text{ kJ/mol} = -97.2 \text{ kJ/mol}$

□ Tetrahedral CFSE = $-0.8 \times 4/9 \times 81 \text{ kJ} = -28.8 \text{ kJ}$

Predict the magnetic moments of the following complexes and on the basis of this data mark them as high spin or low spin complexes

$\text{K}_3[\text{Mn}(\text{NO}_2)_6]$ 2.87 BM = 2 Unpaired electrons, Mn^{3+} , d^4 low spin

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ 1.73 BM = 1 Unpaired electron, Co^{2+} , d^7 low spin

$\text{K}_4[\text{Fe}(\text{CN})_6]$ 0 BM = 0 Unpaired electron, Fe^{2+} , d^6 low spin

A tetrahedral complex absorbs at 545 nm. What is the respective octahedral crystal field splitting (Δ_o)?

$$\begin{aligned}\Delta_t &= \frac{hc}{\lambda} \\ &= \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3 \times 10^8 \text{ m/s})}{545 \times 10^{-9} \text{ m}} \\ &= 3.65 \times 10^{-19} \text{ J}\end{aligned}$$

However, the tetrahedral splitting (Δ_t) is $\sim 4/9$ that of the octahedral splitting (Δ_o).

$$\begin{aligned}\Delta_t &= 0.44\Delta_o \\ \Delta_o &= \frac{\Delta_t}{0.44} \\ &= \frac{3.65 \times 10^{-19} \text{ J}}{0.44} \\ &= 8.30 \times 10^{-18} \text{ J}\end{aligned}$$

Limitations of CFT

- ❑ CFT considers only the metal ion d-orbitals and gives no consideration at all to **other metal orbitals such as s, p_x , p_y and p_z orbitals and the ligands π -orbitals**. Therefore, to explain all the properties of the complexes dependent on the π -ligand orbitals will be outside the scope of CFT.
- ❑ CFT is **unable to account satisfactorily for the relative strengths of the ligands**, e.g., it gives no explanation as to why H_2O appears in the spectrochemical series as a stronger ligand than OH^- .
- ❑ According to CFT, the bond between the metal and ligand is purely ionic. It **gives no account of the partly covalent nature of the metal-ligand bonds**. Thus the effects directly dependent on covalency cannot be explained by CFT.

ISOMERISM IN COORDINATION COMPOUNDS

Compounds having the same molecular formula, but differing in physical and chemical properties are known as isomers. This phenomenon is known as isomerism. The isomers can be identified and distinguished from one another because of difference in their physical and chemical properties

Coordination number and shape



Coordination Number	Shape		Examples
2	Linear		$[\text{CuCl}_2]^-$, $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{AuCl}_2]^-$
4	Square planar		$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{PdCl}_4]^{2-}$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$
4	Tetrahedral		$[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Zn}(\text{NH}_3)_4]^{2+}$, $[\text{CdCl}_4]^{2-}$, $[\text{MnCl}_4]^{2-}$
6	Octahedral		$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{V}(\text{CN})_6]^{4-}$, $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{FeCl}_6]^{3-}$, $[\text{Co}(\text{en})_3]^{3+}$

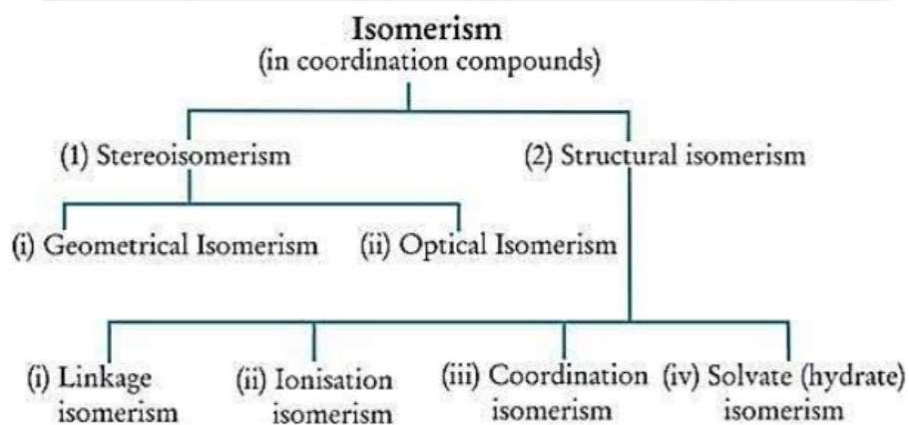
The geometry of a given complex ion depends **both** on the coordination number and the metal ion.

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Types of isomerism



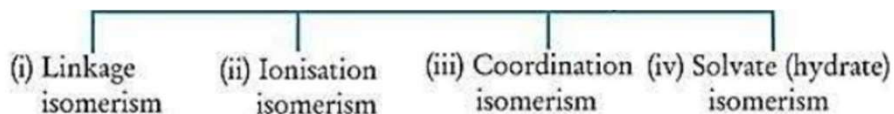
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Structural isomerism



- These isomers have the same molecular formula but different structural arrangement of atoms (or groups of atoms) around the central metal ion



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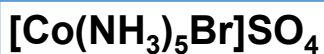
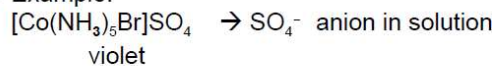
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Ionization isomerism

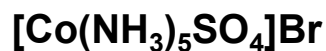


Ionization isomers **are identical except for a ligand has exchanged places with an anion or neutral molecule that was originally outside the coordination complex.** The central ion and the other ligands are identical.

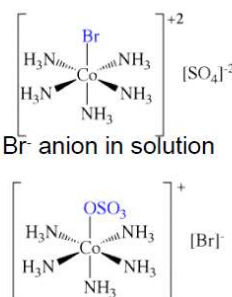
- Example:



and



- $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br} \rightarrow \text{Br}^-$ anion in solution
red



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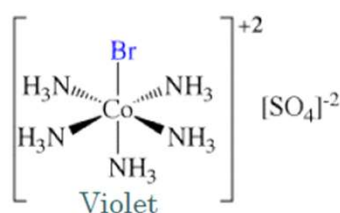
IONIZATION ISOMERISM



Both the compounds have different physical and chemical properties

Red isomer forms an off white precipitate of AgBr with Ag⁺ ions but gives no precipitate with Ba⁺⁺ ions

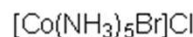
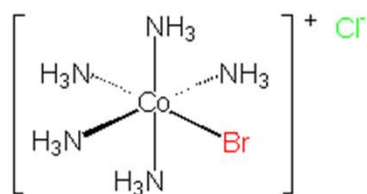
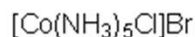
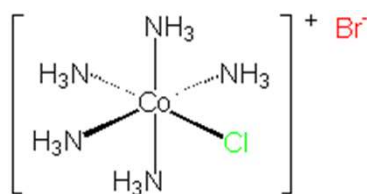
Violet isomer gives precipitate with Ba⁺⁺ ions and no precipitate with Ag⁺ ions



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Ionization isomerism



- ❑ The chloride ion is bound to the cobalt as a **chloro-ligand with the bromide ion as the counter ion.**
- ❑ In the other ionization isomer the bromide is acting as a **bromo-ligand to the cobalt with the chloride acting as the counter ion.**
- ❑ These two isomers are called **pentaamminechlorocobalt(II) bromide** (left) and **pentaamminebromocobalt(II) chloride** (right).

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Ionization isomerism



- Difference between the ionization isomers - **ions generated when each are dissolved in solution.**

- For example, when pentaamminebromocobalt(II) chloride is dissolved in water, Cl^- ions are generated:



- whereas when pentaamminechlorocobalt(II) bromide is dissolved, Br^- ions are generated:



- 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.**

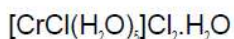
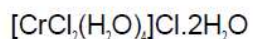
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HYDRATE ISOMERISM



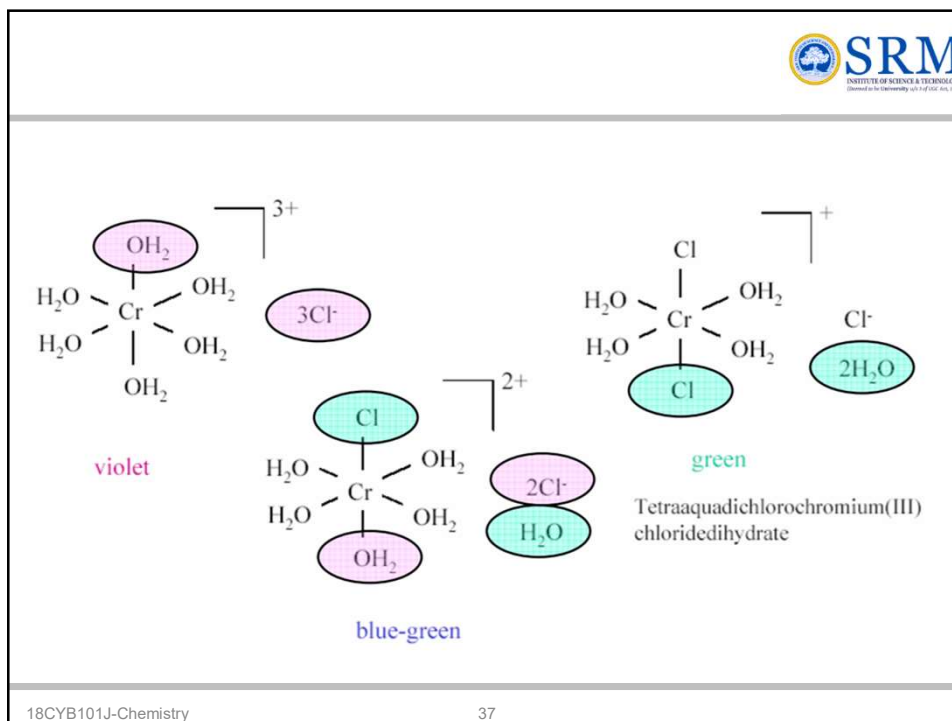
- It arises when different number of water molecules are present inside and outside the co-ordination sphere. This isomerism is illustrated by the 3 isomers that have the formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$




- 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.
- These isomers can lose two, one and no water molecules on dehydration with conc. sulphuric acid respectively

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 SRM

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Coordination isomerism

- ❑ Coordination isomerism occurs 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.**
- ❑ Hence, there are two complex compounds bound together, one with a negative charge and the other with a positive charge.
- ❑ In coordination isomers, the anion and cation complexes of a coordination compound exchange one or more ligands.

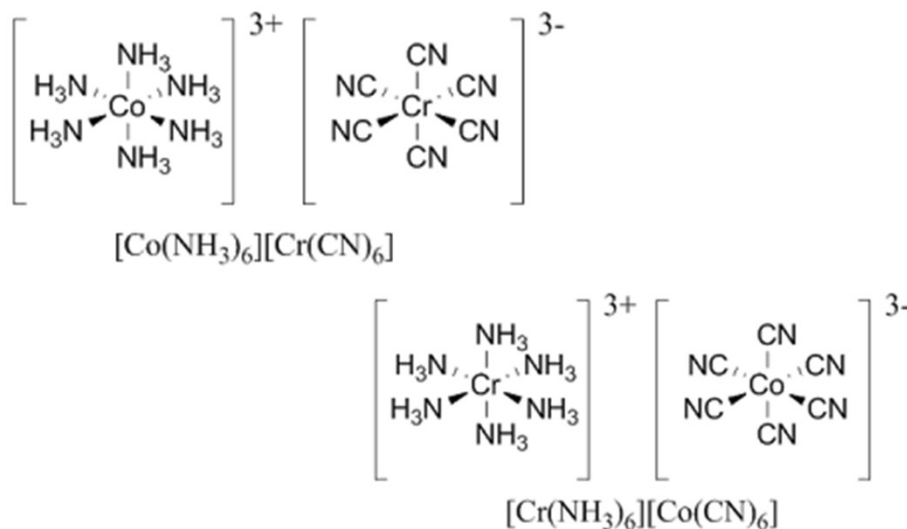
$$[\text{Zn}(\text{NH}_3)_4]^{+2} [\text{CuCl}_4]^{-2}$$

Tetraaminezinc(II)
TetrachloroCuprate(II)

$$[\text{Cu}(\text{NH}_3)_4]^{+2} [\text{ZnCl}_4]^{-2}$$

TetraamineCopper(II)
TetrachloroZincate(II)

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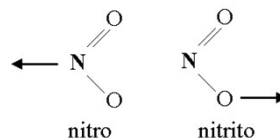


LINKAGE ISOMERISM

- Occurs in co-ordination compounds 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^- .

- Examples:

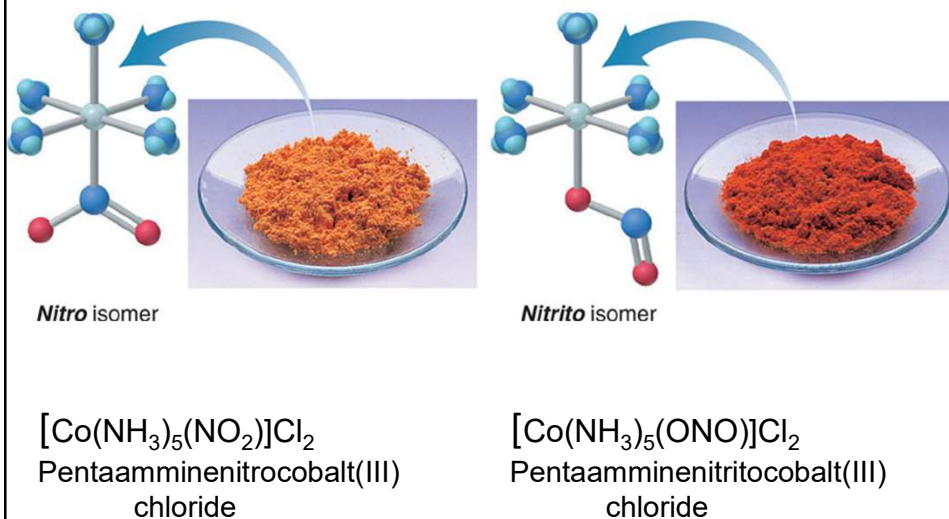
- $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ the nitrito isomer -O attached
- $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ the nitro isomer - N attached.



- $[\text{Co}(\text{NH}_3)_5(\text{NCS})]\text{Cl}_2$ Co-NCS isothiocyanate and
- $[\text{Co}(\text{NH}_3)_5(\text{SCN})]\text{Cl}_2$ Co-SCN thiocyanate

Certain ligands contain more than one atom which could donate an electron pair. In the NO_2^- ion, either N or O atoms could act as the electron pair donor. Thus there is the possibility of isomerism.

Linkage isomerism



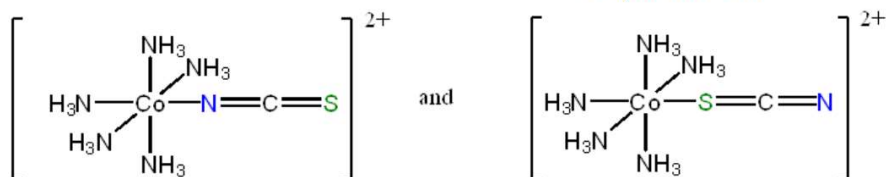
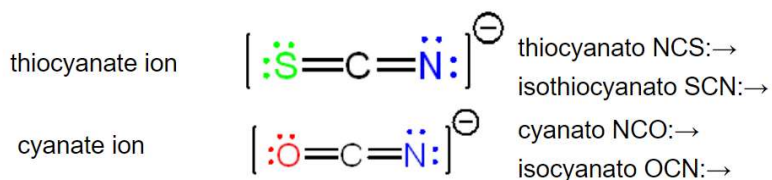
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Linkage isomerism



- Occur when a ligand has two alternative donor atoms.



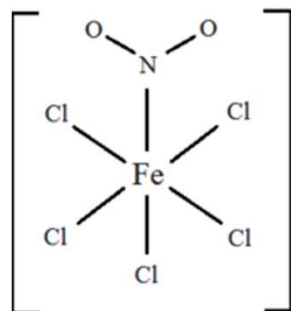
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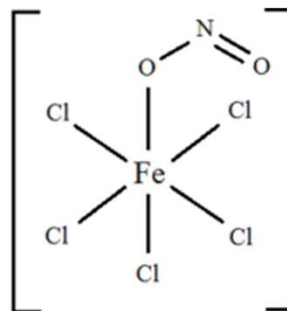
Linkage isomerism



Are $[\text{FeCl}_5(\text{NO}_2)]^{3-}$ and $[\text{FeCl}_5(\text{ONO})]^{3-}$ complex ions linkage isomers of each other? Draw the structure



$[\text{FeCl}_5(\text{NO}_2)]^{3-}$



$[\text{FeCl}_5(\text{ONO})]^{3-}$

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Stereoisomerism

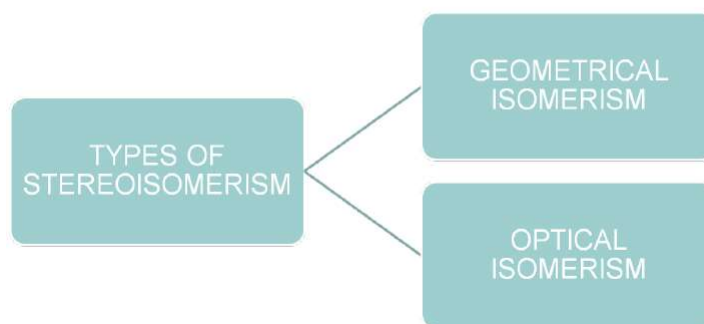


- Compounds are stereoisomer when they contain the same ligands in their coordination spheres but differ in the way that these ligands are arranged in space
- They have the same atom to atom bonding sequence but the atoms differ in their arrangement in space
- They have the same atoms, same sets of bonds but differ in the relative orientation of these bonds

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| STEREOISOMERISM



| GEOMETRICAL ISOMERISM

It is due to ligands occupying different positions around the central metal atom or ion.

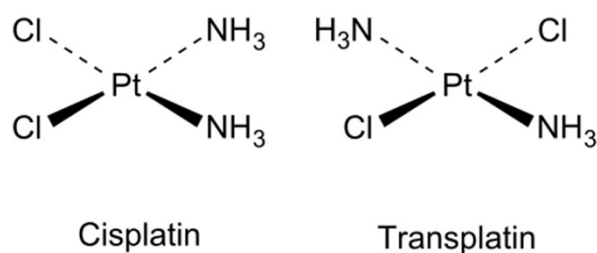
Also known as cis-trans isomerism.

Common in **square planar** and **octahedral** complexes but **not** in **tetrahedral** complexes because all tetrahedral complexes [such as Ma_4 , Ma_2b_2 , $Mabcd$, where a,b,c,d represents ligands] exist in only one geometric form in which all positions are adjacent to each other.

Existence of two different compounds having the molecular formula $[Pt(NH_3)_2Cl_2]$ was used by the father of co-ordination chemistry Alfred Werner to prove that transition metals often have square planar geometries.

Example of Ma_2b_2 type compound

- *cis*- and *trans*- isomers of $[PtCl_2(NH_3)_2]$

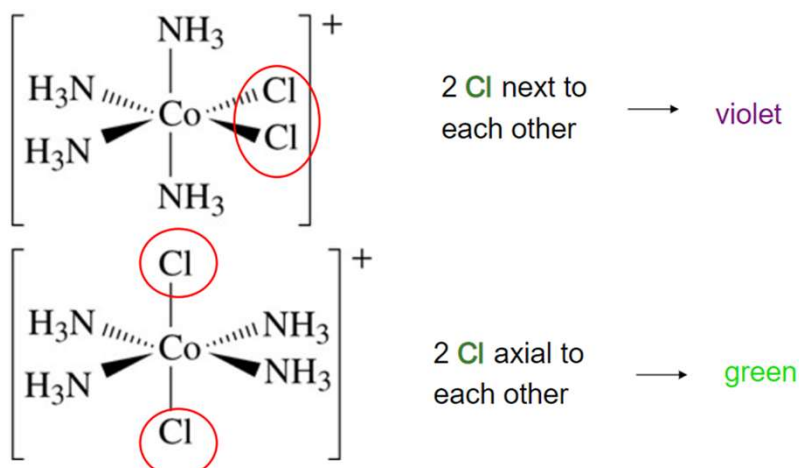


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Stereoisomers, geometric isomers

Octahedral complex. Six coordinate: *cis*- and *trans*- $[Co(NH_3)_4Cl_2]^+$



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Optical isomerism



- 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.
- Common in tetrahedral and octahedral complexes but not in square planar because of the presence of axis of symmetry.
- Very common in octahedral complexes.

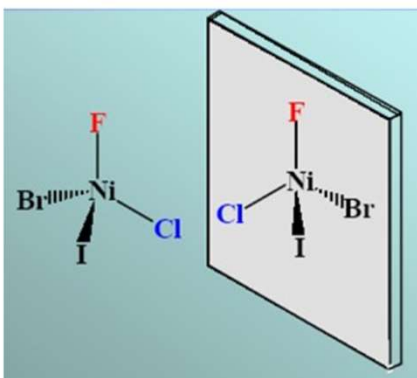
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Optical isomerism



- When a molecule is non-superimposable with its mirror image.
- Example: four different substituents about tetrahedral centre.
- Same physical properties, except direction in which they rotate the plane of polarized light.



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Optical isomerism

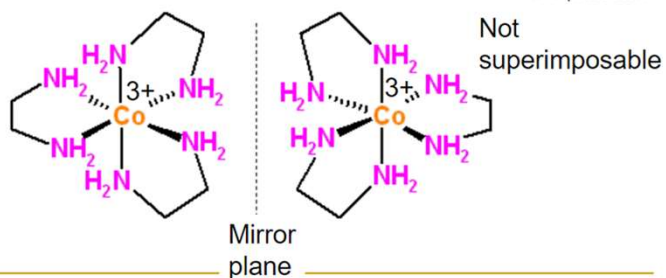


2. Having three bidentate ligands of only one type - gives a propeller-type structure.



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$[M(en)_3]^{n+}$ complexes have optical isomers:

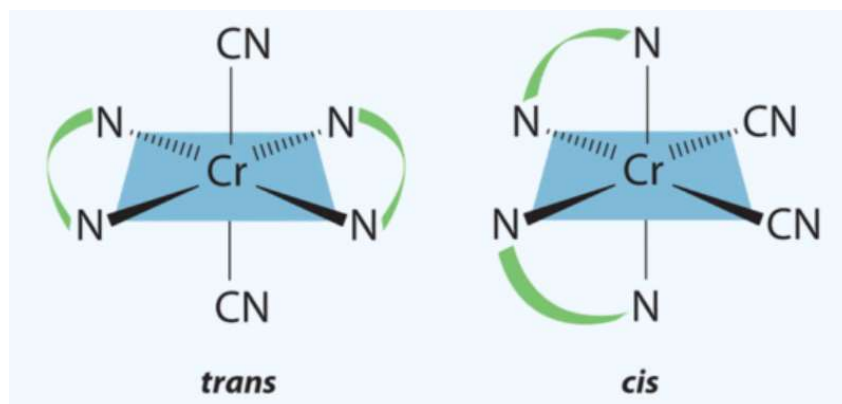


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- Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.



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Practice problem



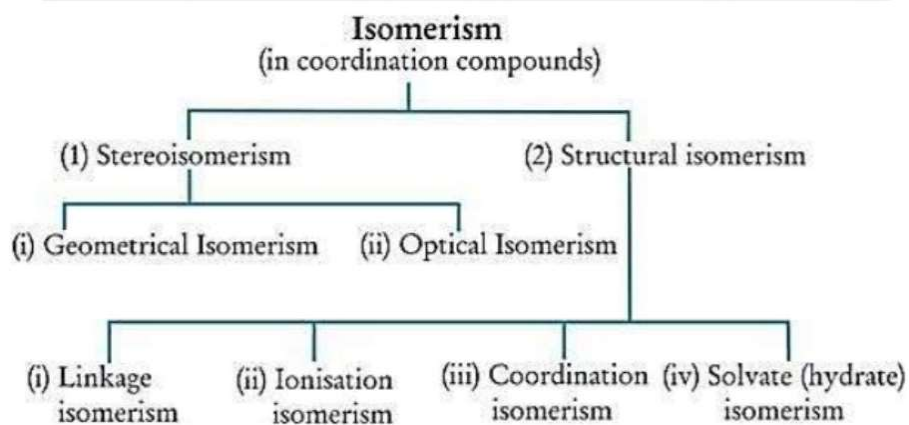
□ **Draw the cis and trans isomers of the following compounds:**

- $(\text{NH}_3)_2\text{IrCl}(\text{CO})$
- $(\text{H}_3\text{P})_2\text{PtHBr}$

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Summary



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Thank you all for your attention

Information presented here were collected from various sources – textbooks, articles, manuscripts, internet and newsletters. All the researchers and authors of the above mentioned sources are greatly acknowledged.