

**Chapter-22****Coordination Chemistry (Structural Isomerism)**

Arijit Das

Department of Chemistry, Bir Bikram Memorial College, Agartala, Tripura, India

Email: [arijitdas78chem@gmail.com](mailto:arijitdas78chem@gmail.com)**Isomerism in co-ordination compounds (iso-equal, meros – parts):**

Two or more compounds having same molecular formula (same molecular weight) but different structural formula and property are known as *isomers* and the phenomenon is called *isomerism*.

Isomerism is common in organic compounds but less common in inorganic compounds.

Isomerism in co-ordination compounds depends upon following factors.

1. Variety of bond 2. Multiplicity of molecular arrangement 3. Complexity of stereochemical relationship

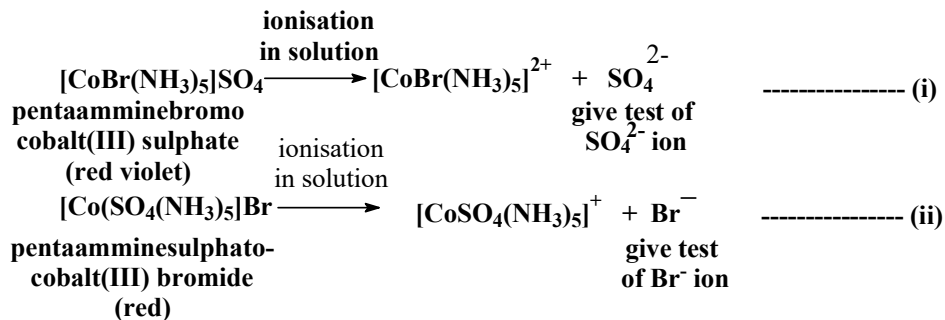
**Types of isomerism:**

<b>Structural isomerism (molecules having different structural arrangement)</b>	<b>Stereoisomerism (molecules differ by spatial arrangement around the central metal atom)</b>
1) Ionisation isomerism 2) Hydrate isomerism 3) Co-ordination isomerism 4) Linkage or structural salt isomerism 5) Co-ordination position isomerism 6) Polymerisation isomerism 7) Ligand isomerism 8) Nuclear coordination polymerization isomerism 9) Valence isomerism	1) Geometrical isomerism  2) Optical isomerism

**Structural isomerism:** Molecules having same molecular formula (molecular weight) but different in structural arrangement are called structural isomers and the whole phenomena regarding as structural isomerism.

**1. Ionisation isomerism:** This type of isomerism is due to interchange of groups or ions between the co-ordination sphere and the ionization sphere. The ions which are present in the ionization sphere come in the free state after dissociation or ionization of the compounds in solution and thus give positive response under different analytical test. The ions which are present in the coordination sphere (within the 3<sup>rd</sup> bracket) do not undergo free state in solution and thus give

negative response in different analytical test or chemical reaction. These isomers give different ions in solution as shown below –



Eq. (i) give positive test with 5%  $\text{BaCl}_2$  solution because sulphate ( $\text{SO}_4^{2-}$ ) ion present in the free state which reacts with 5%  $\text{BaCl}_2$  solution to give white precipitate of  $\text{BaSO}_4$ . It doesn't give positive test with silver nitrate ( $\text{AgNO}_3$ ) solution due to absence of  $\text{Br}^-$  ion in the ionization sphere.

Eq. (ii) give positive test with silver nitrate ( $\text{AgNO}_3$ ) solution because  $\text{Br}^-$  ion present in the free state which reacts with  $\text{AgNO}_3$  solution to give yellow precipitate of  $\text{AgBr}$ . It doesn't give positive test with 5%  $\text{BaCl}_2$  solution due to absence of sulphate ( $\text{SO}_4^{2-}$ ) ion in the ionization sphere.

**Other examples:**

- (i)  $[\text{CoCl}_2(\text{NH}_3)_4]\text{NO}_2$  and  $[\text{CoCl}(\text{NO}_2)(\text{NH}_3)_4]\text{Cl}$
- (ii)  $[\text{CoNO}_3(\text{NH}_3)_5]\text{SO}_4$  and  $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{NO}_3$
- (iii)  $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$  and  $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$
- (iv)  $[\text{CoCl}(\text{NO}_2)(\text{NH}_3)_4]\text{Cl}$  and  $[\text{CoCl}_2(\text{NH}_3)_4]\text{NO}_2$

**2. Hydrate isomerism:** This type of isomerism is due to different position of water molecules in a complex. Water molecules which are present in the ionization sphere absorb by dehydrating agent conc.  $\text{H}_2\text{SO}_4$  but water molecules which are present in the coordination sphere donot absorb when react with conc.  $\text{H}_2\text{SO}_4$ .

e.g.  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  gives following three types of hydrate isomers.

- i)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ : Do not loss water molecule after reaction with  $\text{H}_2\text{SO}_4$  (no water molecule present in the ionization sphere) and give positive test with  $\text{AgNO}_3$  due to presence of three chloride ( $\text{Cl}^-$ ) ions within the ionization sphere.
- ii)  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ : It loses one molecule of  $\text{H}_2\text{O}$  on reaction with  $\text{H}_2\text{SO}_4$  and  $2\text{Cl}^-$  give  $\text{AgNO}_3$  test.
- iii)  $[\text{CrCl}_2 \cdot (\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ : It loses two molecules of  $\text{H}_2\text{O}$  on reaction with  $\text{H}_2\text{SO}_4$  and one  $\text{Cl}^-$  gives  $\text{AgNO}_3$  test.

**Other examples:**

- i)  $[\text{CoCl}(\text{en})_2(\text{H}_2\text{O})]\text{Cl}_2$  and  $[\text{CoCl}_2(\text{en})_2]\text{Cl} \cdot \text{H}_2\text{O}$
- ii)  $[\text{CoCl}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Cl}_2$  and  $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl} \cdot \text{H}_2\text{O}$
- iii)  $[\text{CrCl}_2(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})_2]\text{Cl}$  and  $[\text{CrCl}_3(\text{C}_5\text{H}_5\text{N})_2\text{H}_2\text{O}]\text{H}_2\text{O}$

**Key point:**

Due to exchange of water molecules with ions or groups remember that coordination number must remain same before and after exchange.

**3. Coordination isomerism:** This type of isomerism occurs when there is an exchange of ligands between two coordination spheres that is they differ in the coordination of ligand due to such interchange.

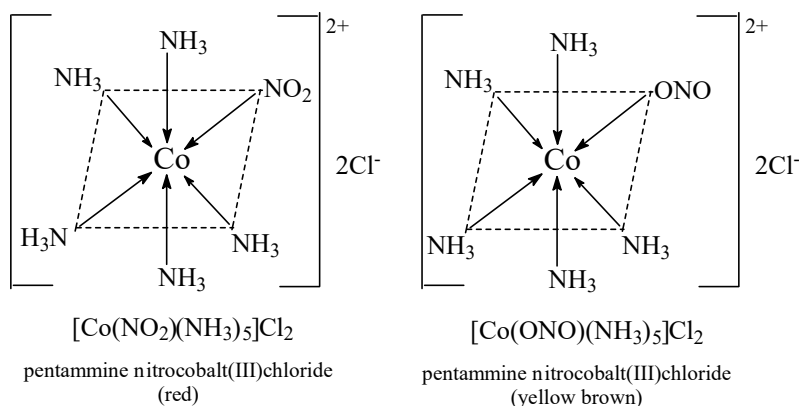
**Examples:**

- (i)  $[\text{Cu}(\text{NH}_3)_4]^{2+} [\text{PtCl}_4]^{2-}$  and  $[\text{Pt}(\text{NH}_3)_4]^{2+} [\text{CuCl}_4]^{2-}$
- (ii)  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
- (iii)  $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{CN})_2(\text{NH}_3)_4][\text{Cr}(\text{CN})_4(\text{NH}_3)_2]$
- (iv)  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$  and  $[\text{PtCl}(\text{NH}_3)_3][\text{PtCl}_3(\text{NH}_3)]$

**Key points:**

- i) Metal ions of both coordination spheres may be same or different but their oxidation state and coordination number will remain same.
- ii) During writing coordination isomers first put positive coordination sphere followed by negative one.
- iii) During counting number of coordination isomers exclude neutral coordination sphere (if any).
- iv) In case of same metal ions in both the coordination spheres only partial exchange of ligands between two coordination spheres should take place.
- v) In case of different metal ions in both the coordination spheres partial exchange as well as fully exchange of ligands between two coordination spheres should take place.

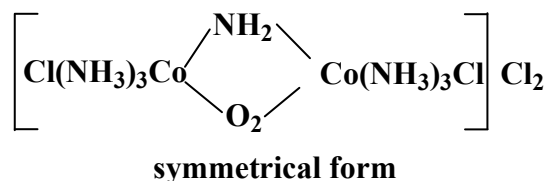
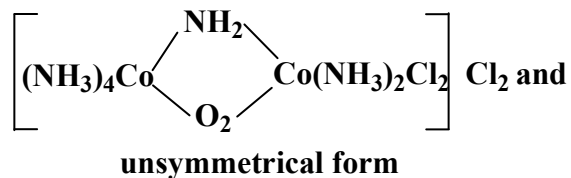
**4. Linkage isomerism :** This type of isomerism occurs when in coordination compound there is a presence of Ambidentate ligand (differ in metal-ligand linkage), e.g.



**Other examples of Ambidentate ligand:**

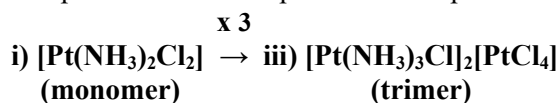
- (i)  $\text{CN}^- \rightarrow$  cyano (bonded by 'C')
- (ii)  $\text{NC}^- \rightarrow$  isocyano (bonded by 'N')
- (iii)  $\text{SCN}^- \rightarrow$  thiocyano (bonded by S)
- (iv)  $\text{NCS}^- \rightarrow$  isothiocyano (bonded by N)

**5. Coordination position isomerism :** This type of isomerism occurs in polynuclear compounds in which coordination group (not bridging group) may be present in the same number but arrange differently with respect to the different metal ion as –

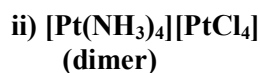


In above example, ammonia and chloride ion are present in the same number but arrange differently with respect to the different cobalt ion.

**6. Polymerisation isomerism** : Polymer is nothing but the multiple unit of monomer. This type of isomerism is due to compounds having same stoichiometric composition but whose molecular compositions are multiples of the simplest stoichiometric arrangement (monomer) such as –

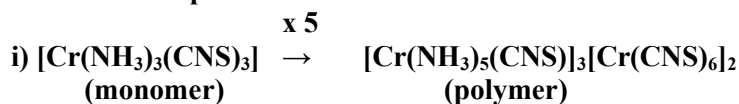


↓ x 2



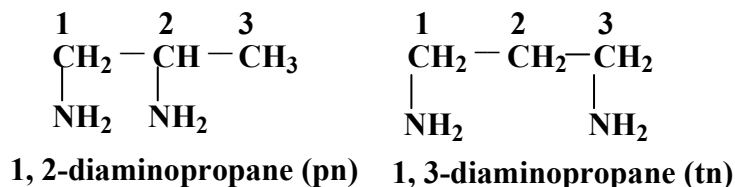
From the above example we can see that (ii), (iii) structures are polymers of (i). Here we have difference in arrangements as well as a multiplication of molecular weight.

**Another example is**

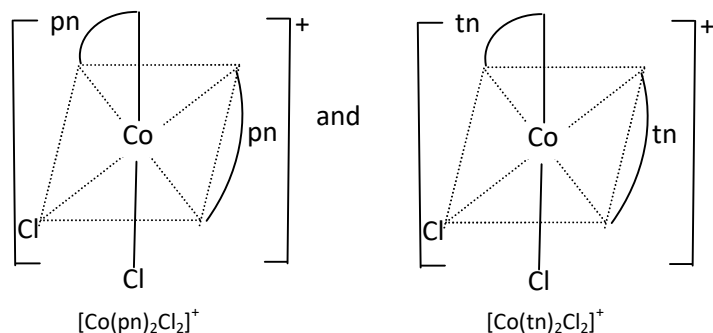


**7. Ligand isomerism** : It is found that many ligands also have isomeric forms. So when these ligands are associated to form complexes then these complexes are treated as ligand isomer of each other and the whole phenomena regarded as ligand isomerism,

e.g. diaminopropane has two positional isomers (functional group same but their positions are different) as 1,2-diaminopropane(pn) and 1,3-diaminopropane(tn) form as given below –



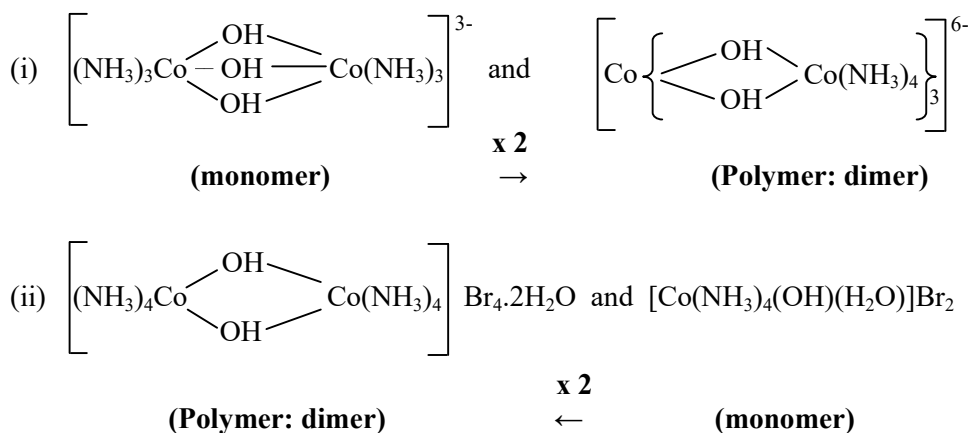
When these pn and tn form complexes with same metal ions like as  $[\text{Co}(\text{pn})_2\text{Cl}_2]^+$  and  $[\text{Co}(\text{tn})_2\text{Cl}_2]^{2+}$  then these complexes are treated as ligand isomer of each other as follows:



Another example is  $[\text{Co}(\text{en})_2\text{Cl}(\text{chloroaniline})]^+$  which have three ligand isomers due to three positional isomers of chloroaniline such as 'ortho', 'meta' and 'para'.

### 8. Nuclear co-ordination polymerization isomerism:

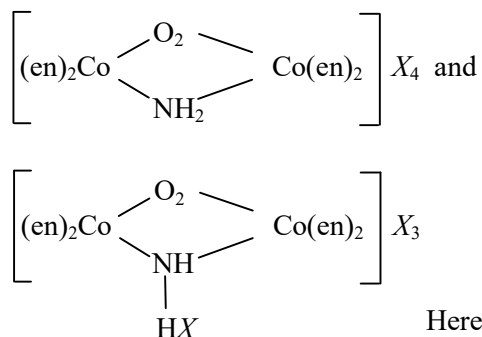
This type of isomerism is due to the different number of nuclei present in bridged complexes having polymeric relation to each other, e.g.



### Key points:

- i) Polynuclear
- ii) Bridged complexes
- iii) Polymeric relation

**9. Valence isomerism :** This type of isomerism is due to different bonding of a polynuclear complex, e.g.



## Related Questions

**Q.1. Complex (A) has a composition of  $H_{12}O_6Cl_3Cr$ . If the complex on treatment with conc.  $H_2SO_4$  loses 13.5% of its original mass, the correct molecular formula of (A) is [Given : atomic mass of Cr = 52 amu and Cl = 35 amu]**

- a)  $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$   
 b)  $[Cr(H_2O)_6]Cl_3$   
 c)  $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$   
 d)  $[Cr(H_2O)_3Cl_3] \cdot 3H_2O$

**Ans. (a)**

Complex (A) =  $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

Generally, conc.  $H_2SO_4$  can act as oxidizing agent as well as dehydrating agent. Here,  $H_2SO_4$  act as dehydrating agent.

Molar mass of complex = 266.5 g/mol

On reaction with conc.  $H_2SO_4$  the mass by complex

$$= \frac{13.5}{100} \times 266.5 = 35.9775 = 36 \text{ g}$$

It means that 2 moles of  $H_2O$  are present in complex.

$$[\because \text{Molar mass of } H_2O = 18 \text{ g/mol}]$$

Then, formula of complex is



**Q.2. The number of isomers possible for  $[Pt(en)(NO_2)_2]$  is**

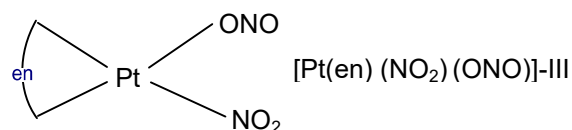
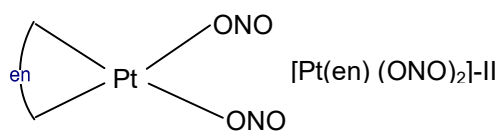
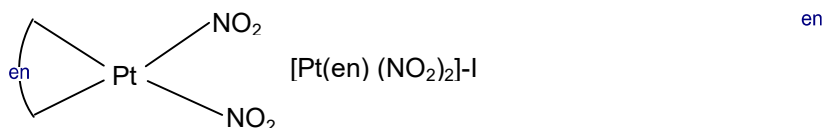
- (a) 3            (b) 2            (c) 4            (d) 1

**Ans. (a)**

Total number of possible isomers for  $[Pt(en)(NO_2)_2]$  are 3.

$NO_2$  — ambidentate ligand, en — bidentate ligand and coordination number is 4.

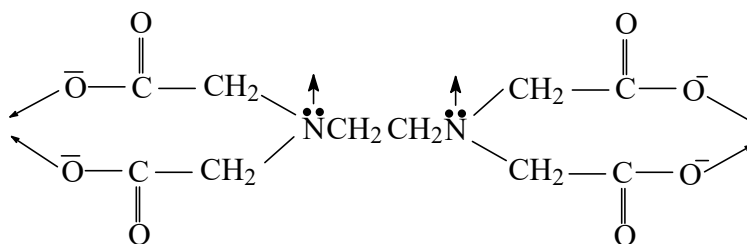
Structures are as follows:



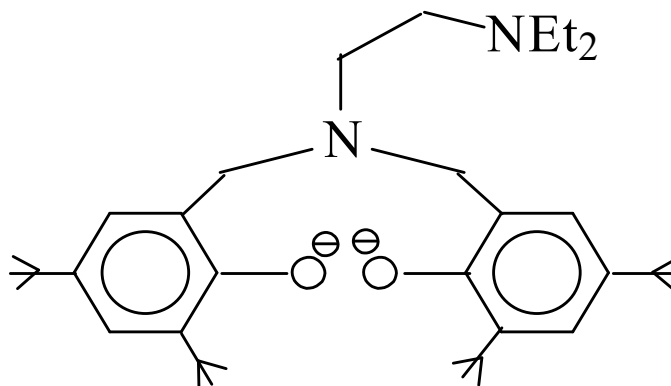
**Q.3. The total number of coordination sites in ethylenediaminetetraacetate [EDTA<sup>4-</sup>] is .....**

**Ans. (6) (see chapter 21 Coordination Chemistry: Introduction)**

EDTA<sup>4-</sup> is ethylenediaminetetraacetate anion. It is a polyprotic acid containing four carboxylic acid groups and two amine groups with lone – pair electrons that chelate calcium and several other metal ions, it has six coordination sites. It is a hexadentate ligand.



**Q.4. The following ligand is**



a) hexadentate  
c) bidentate

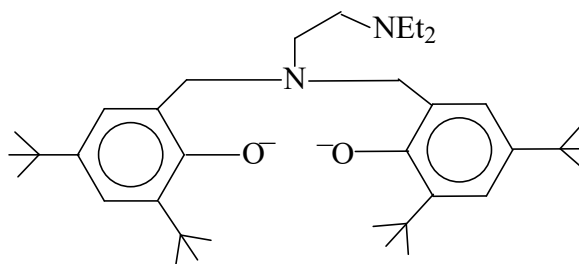
b) tetradentate  
d) tridentate

**Ans. (b) (see chapter 21 Coordination Chemistry: Introduction)**

**N.B.** Denticity or ligand is defined as donor sites of number of ligating groups.

The given ligand is tetradentate. It contains four donor atoms. It can bind through two nitrogen and two oxygen atom to the central metal ion.

Ligand bound to the central atom or ion through coordinate bond in the coordination entity. It acts as a Lewis base.



**Q.5. The coordination numbers of Co and Al in  $[\text{CoCl}(\text{en})_2]\text{Cl}$  and  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$ , respectively, are (en = ethane-1, 2-diamine)**

- a) 5 and 3    b) 3 and 3  
c) 6 and 6    d) 5 and 6

**Ans. (d)**

**N.B.:** The total number of ligands to which the metal is directly attached is called coordination number.

The coordination numbers of Co and Al in  $[\text{Co}(\text{Cl})(\text{en})_2]\text{Cl}$  and  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$  are 5 and 6 respectively.

In first complex  $[\text{Co}(\text{Cl})(\text{en})_2]\text{Cl}$ , 'en' is a bidentate ligand and 'Cl' is a unidentate ligand.

For  $[\text{Co}(\text{Cl})(\text{en})_2]\text{Cl}$ , coordination number =  $1 + 2 \times 2 = 1 + 4 \Rightarrow 5$

So, the coordination number is 5.

For  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$ , ' $\text{C}_2\text{O}_4^{2-}$ ' is a didentate ligand.

Coordination number =  $3 \times 2 = 6$ .

Hence, coordination number is 6.

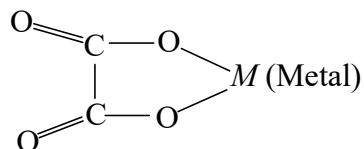
**Q.6. The coordination number of Th in  $\text{K}_4[\text{Th}(\text{C}_2\text{O}_4)_4(\text{OH}_2)_2]$  is ( $\text{C}_2\text{O}_4^{2-} = \text{Oxalato}$ )**

- a) 14    b) 10    c) 8    d) 6

**Ans. (b)**

Coordination number is defined as the total number of ligands to which the metal is directly attached.

Here,  $\text{C}_2\text{O}_4^{2-}$  is a bidentate ligand,



and  $\text{H}_2\text{O}$  is a monodentate ligand,  $\text{H}_2\ddot{\text{O}}: \longrightarrow \text{M}$

So, total number of donor sites offered by  $\text{C}_2\text{O}_4^{2-}$  and  $\text{H}_2\text{O}$  ligands around Th (IV) =  
Coordination number of Th (IV) =  $4 \times 2$  (by  $\text{C}_2\text{O}_4^{2-}$ ) +  $2 \times 1$  (by  $\text{H}_2\text{O}$ ) = 10

**Q.7. Which of the following pairs represents linkage isomers?**

- a)  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$  and  $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$   
b)  $[\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2]$  and  $[\text{Pd}(\text{PPh}_3)_2(\text{SCN})_2]$   
c)  $[\text{Co}(\text{NH}_3)_5]\text{NO}_3\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$   
d)  $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$  and  $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$

**Ans: (b) contains  $\text{SCN}^-$  as ambidentate ligand**



**Q.8. The coordination number and the oxidation state of the element 'E' in the complex  $[E(en)_2(C_2O_4)]NO_2$  (where (en) is ethylene diamine) are, respectively**

- a) 6 and 2    b) 4 and 2    c) 4 and 3    d) 6 and 3

**Ans: (d) coordination number - 06 and oxidation state - 03**

**Q.9. One mole of the complex compound  $Co(NH_3)_5Cl_3$  having coordination number 6 gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of  $AgNO_3$  solution to yield two moles of  $AgCl(s)$ . The structure of the complex is**

- a)  $[Co(NH_3)_5Cl]Cl_2$   
 b)  $[Co(NH_3)_3Cl_3].2NH_3$   
 c)  $[Co(NH_3)_4Cl_2]Cl.NH_3$   
 d)  $[Co(NH_3)_4Cl]Cl_2.NH_3$

**Ans: a)  $[Co(NH_3)_5Cl]Cl_2$**

Here, coordination number is 6 and two  $Cl^-$  ions are present in the ionization sphere which reacts with  $AgNO_3$  solution to yield two moles of  $AgCl(s)$ .

**Q.10. Type of isomerism shown by  $[Cr(NH_3)_5NO_2]Cl_2$  is**

- a) optical                      b) ligand  
 c) geometrical                d) linkage

**Ans: d)  $[Cr(NH_3)_5NO_2]Cl_2$  exhibits linkage isomerism due to presence of  $NO_2^-$  as ambidentate ligand.**

### Reference Books:

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- 2. Coordination chemistry, Joan Ribas Gispert*
- 3. Coordination Chemistry, 20: Invited Lectures Presented at the 20th International Conference on Coordination Chemistry, Calcutta, India, 10-14 December 1979, D. Banerjea*
- 4. Comprehensive Coordination Chemistry III, Gerard Parkin, Edwin C Constable, Lawrence Que*
- 5. [https://chem.libretexts.org/Bookshelves/Inorganic\\_Chemistry/Supplemental\\_Modules\\_and\\_Websites\\_\(Inorganic\\_Chemistry\)/Coordination\\_Chemistry/Complex\\_Ion\\_Equilibria/Stability\\_of\\_Metal\\_Complexes\\_and\\_Chelation](https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Websites_(Inorganic_Chemistry)/Coordination_Chemistry/Complex_Ion_Equilibria/Stability_of_Metal_Complexes_and_Chelation)*

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