# **Coordination Compounds**

#### ONE MARK QUESTIONS:

- Q.1Write the formula forTetraamineaquachloridocobalt(III) chloride
- Q.2 Write the IUPAC name of [Co (NH<sub>3</sub>)<sub>4</sub> Br<sub>2</sub>]<sub>2</sub> [Zn Cl<sub>4</sub>]
- Q.3 Which of these cannot act as ligand and why: NH<sub>3</sub>, H<sub>2</sub>O, CO, CH<sub>4</sub>. Give reason?
- Q.4 How many EDTA (lethylendiamine tetra acetic acid) molecules are required to make an octahedral complex with a  $Ca^{2+}$  ion.
- Q.5 Why tetrahedral complexes do not exhibit geometrical isomerism?
- Q.6 What is the hybridisation of central metal ion and shape of Wilkinson's catalyst?
- Q.7 Specify the oxidation numbers of the metals in the following coordination entities:
- (i)  $[Co(H_2O)(CN)(en)_2]^{2+}$  and
- (ii)  $[CoBr_2(en)_2]^+$
- Q.8 Draw the structure of optical isomers of  $[Co(en)_3]^{3+}$ .
- Q.9 Name the types of isomerism exhibited by  $[Co(NH_3)_5(NO_2)](NO_3)_2$
- Q.10 Write the formula of Amminebromidochloridonitrito-N-platinate(II) ion
- Q.11 which one is more stable complex among(i)  $[Fe(H_2O)_6]^{3+}$  (ii)  $[Fe(NH_3)_6]^{3+}$  (iii)  $[Fe(C_2O_4)_3]^{3-}$
- Q.12 How many ions are produced from the complex Co(NH<sub>3</sub>)<sub>6</sub>Cl<sub>2</sub> in solution?
- Q.13 What do you meant by degenerate d-orbitals?
- Q.14 Out of the following two coordination entities which is chiral (optically active)? (a) cis-[CrCl2 (ox)<sub>2</sub>]<sup>3-</sup> (b) trans-[CrCl2 (ox)<sub>2</sub>]<sup>3-</sup>
- Q.15 The spin only magnetic moment of  $[MnBr_4]^{2-}$  is 5.9 BM. Predict the geometry of the complex ion?
- Q.16 What is the oxidation state of Ni in  $[Ni(CO)_4]$ .
- Q.17 What is the magnetic behavior of  $[Ni(CN)_4]^{2-}$ .
- Q.18 Name the metal ion present in vitamin  $B_{12}$ .
- Q.19 Name the isomerism shown by complex  $K[Cr(H_2O)_2(C_2O_4)_2]$
- Q.20 Name the compound used for inhibiting the growth of tumours. (cancer treatment)

#### TWO MARK QUESTIONS:

- Q.1Write the IUPAC names of the following coordination compounds:
- (i)  $[Pt(NH_3)_2Cl(NO_2)]$
- (ii)  $K_3 [Cr(C_2O_4)_3]$
- Q.2 A cationic complex has two isomers A & B. Each has one  $Co^{3+}$ , five NH<sub>3</sub>, one Br and one  $SO_4^{2-}$ . A gives a white precipitate with BaCl<sub>2</sub> solution while B gives a yellow precipitate with AgNO<sub>3</sub> solution.

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- (a) What are the possible structures of the complexes A and B?
- (a) Write the name of structural isomerism shown by A and B.
- Q.3 FeSO<sub>4</sub> solution mixed with  $(NH_4)_2SO_4$  solution in 1 : 1 molar ratio gives the test of Fe<sup>2+</sup> ion but CuSO<sub>4</sub> solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu<sup>2+</sup> ion. Explain why?
- Q.4 What is meant by ambidentate ligands? Give two examples.
- Q.5  $[Co(NH_3)_6]^{3+}$  is diamagnetic whereas  $[Co(F_6)]^{3-}$  is paramagnetic. Give reasons.
- Q.6  $[Cr(NH_3)_6]^{3+}$  is paramagnetic while  $[Ni(CN)_4]^{2-}$  is diamagnetic. Explain why?
- Q.7 Draw figure to show the splitting of d orbitals in an octahedral crystal field. How is the magnitude of  $\Delta_0$  affected by
  - (i) Nature of ligand.
  - (ii) Oxidation State of metal ion.
- Q.8 Metal carbonyl are much more stable than normal complexes, why?
- Q.9 Give evidence that [Co(NH<sub>3</sub>)<sub>5</sub>Cl]SO<sub>4</sub> and [Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>]Cl are ionization isomers.
- Q.10 Write the formulas for the following coordination compounds and name the isomerism shown by them:
  - i. potassium tetracyanonickelate(II)
  - ii. tris(ethane-1,2-diamine) chromium(III) chloride

#### THREE MARK QUESTIONS:

- Q.1 How many geometrical isomers are possible in the following coordination entities?
  - (i)  $[Cr(C_2O_4)_3]^{3-}$  (ii)  $[Co(NH_3)_3Cl_3]$
- Q.2 (a) Write the IUPAC name of  $[Ti(H_2O)_6]^{+3}$ .
  - (b)  $[Ti(H_2O)_6]^{+3}$  is coloured why?
  - (c) A Complex having scandium in +3 oxidation-state was found colorless why?
- Q.3 (a) Write IUPAC name of  $[Co(en)_3]^{3+}$ 
  - (b)  $[NiCl_4]^{2^-}$  is paramagnetic while  $[Ni(CO)]_4$  is diamagnetic though both are tetrahedral. Why?
  - (c) Explain why  $K_3[Fe(CN)_6]$  is more stable than  $K_4[Fe(CN)_6]$ .
- Q.4 (a) What is the hybridization state of nickel in  $[Ni(CN)_4]^{2-}$ 
  - (b) Draw the structure of  $[Ni(CN)_4]^{2-}$
  - (c) A solution of  $[Ni(H_2O)_6]^{2+}$  is green but a solution of  $[Ni(CN)_4]^{2-}$  is colourless. Explain.
- Q.5 Explain  $\left[\text{Co}(\text{NH}_3)_6\right]^{3+}$  is an inner orbital complex whereas  $\left[\text{Ni}(\text{NH}_3)_6\right]^{2+}$  is an outer orbital complex.

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- Q.6 For the complexes (i)  $[Ni(CN)_4]^{2-}$  (ii)  $[Ni(CI)_4]^{2-}$  (iii)  $[Ni(CO)_4]$  Identify:
  - (a) The oxidation No. of nickel
  - (b) The hybrid orbitals and the shape of the complexes
- Q.7 Specify the (i) oxidation numbers (ii) coordination numbers and (iii) IUPAC name of the following coordination entities:
- (a)  $[Co(H_2O)(CN)(en)_2]^{2+}$
- (b)  $[PtCl_4]^{2-}$
- Q.8 Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:
- (a)  $[Fe(CN)_6]^{4-}$
- (b)  $[FeF_6]^{3-}$
- Q.9 Dimethyl glyoxime is added to alcoholic solution of NiCl<sub>2</sub>. When ammonium hydroxide is slowly added to it, a rosy red precipitate of a complex appears.
- (a) Give the str. of the complex showing hydrogen bond.
- (b) Give oxidation state and hybridization of central metal ion.
- (c) Identify whether it is paramagnetic or diamagnetic.
- Q.10 Draw all the isomers (geometrical and optical) of:
  - (a)  $[CoCl_2(en)_2]^+$
  - (b)  $[Co(NH_3)Cl(en)_2]^{2+}$

#### FIVE MARK QUESTIONS:

Q.1 For the complex [Fe(en) $_2$ Cl $_2$ ]Cl identify :

(2009)

- (a) the oxidation No. of Iron.
- (b) the hybrid orbitals and the shape of the complex.
- (c) the magnetic behavior of the complex.
- (d) No. of geometrical isomers.
- (e) whether there is an optical isomer also
- (f) name of the complex.
- Q.2 State a reason for each of the following situations
- (a) Co<sup>2+</sup> ion is easily oxidized to Co<sup>3+</sup> in the presence of strong ligand. (2010,12)
- (b) CO is a stronger complexing reagent than NH<sub>3</sub>. (2009,12)
- (c) The molecular shape of  $[Ni(CO)_4]$  is not the same as that of  $[Ni(CN)_4]^{2-}$ . (2012)
- (d) Ni does not form low spin octahedral complexes. (2009,10)



(e) The  $\pi$  complexes are known for the transition metals only.

(2009, 10)

Q.3 Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronicconfiguration and coordination number. Also give stereochemistry and magnetic moment of the complex:

- $(i)K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$
- (ii)  $[Co(NH_3)_5Cl]Cl_2$
- (iii)CrCl<sub>3</sub>(py)<sub>3</sub>

Q.4 (i) Write the IUPAC name and type of isomerism shown by following complex compounds

- a)  $[Co(NH_3)_5(NO_2)](NO_3)_2$
- b)  $[Pt(NH_3)(H_2O)Cl_2]$

(ii) Write all the geometrical isomers of [Pt(NH<sub>3</sub>)(Br)(Cl)(py)] and how many of these will exhibit optical isomers

Q.5 (i) If to an aqueous solution of  $CuSO_4$  in two tubes, we add ammonia solution in one tube and  $HCl_{(aq)}$  to the other tube, how the colour of the solutions will change? Explain with the help of reaction.

(ii) Write the IUPAC name of complex compounds formed during the process

(Answers)

UNIT- 09

Coordination Compounds

Answers(one mark questions)

- Ans.1  $[Co(NH_3)_4(H_2O)Cl]Cl_2$
- Ans.2 Tetraamminedibromocobalt (III) tetrachlorozincate (II)
- Ans.3 CH<sub>4</sub> can't act as a ligand due to absence of lone pair of electron.
- Ans.4 EDTA is a hexadentate ligand therefore only one EDTA molecule is required.

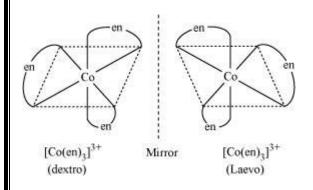
Ans.5 Because relative position of ligands attached to central atom are same with respect to one another

Ans.6 Wilkinson's catalyst is (PH<sub>3</sub>P)<sub>3</sub>RhCl. In this Rh has dsp<sup>2</sup> hybridisation and square planar shape.

Ans.7 (i) +3 (ii) +3

Ans.8





Ans 9. It can show linkage isomerism.

 $[Co(NH_3)_5(NO_2)](NO_3)_2$  and  $[Co(NH_3)_5(ONO)](NO_3)_2$ 

It can also show ionization isomerism.

 $[Co(NH_3)_5(NO_2)](NO_3)_2$  and  $[Co(NH_3)_5(NO_3)](NO_3)(NO_2)$ 

Ans 10.[Pt(NH<sub>3</sub>)Br Cl (NO<sub>2</sub>)]

Ans 11.  $[Fe(C_2O_4)_3]^{3-}$  (due to chelation)

Ans 12. The given complex can be written as  $[Co(NH_3)_6]C_{2}$ 

Thus  $[Co(NH_3)_6]^+$  along with two Cl<sup>-</sup>ions are produced.

Ans.13 d-orbitals having same energy are called as degenerate d- orbitas.

Ans. 14 *cis*-[CrCl2 (ox)<sub>2</sub>] $^{3-}$ 

Ans. 15 Tetrahedral (sp<sup>3</sup>)

Ans 16 Zero (0)

Ans 17. Diamagnetic

Ans 18. Cobalt (Co<sup>3+</sup>)

Ans 19. Both geometrical (*cis-, trans-*) isomers for  $K[Cr(H_2O)_2(C_2O_4)_2]$  can exist. Also, optical isomers for *cis-*iso ner exist.

Ans 20.compounds of platinum (for example, cis-platin)

Answers(two mark questions)

Ans. 1

(i) [Pt(NH<sub>3</sub>)<sub>2</sub>Cl(NO<sub>2</sub>)] Diaminechloridonitro(o)platinum(II)

(ii)  $K_3$  [Cr( $C_2$   $O_4$ )<sub>3</sub>] Potassium trioxalatochromate(III)

Ans. 2

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- (a)  $[CO (NH_3)_5Br]SO_4$ and  $[CO (NH_3)_5SO_4]Br$
- (b) Ionisation Isomerism

#### Ans. 3

When  $FeSO_4$  and  $(NH_4)_2SO_4$  solution are mixed in 1 : 1 molar ratio, a double salt is formed. It has the formula  $FeSO_4$   $(NH_4)_2SO_4$  .6  $H_2O$ . In aqueous solution, the salt dissociates in to its constituent ions.

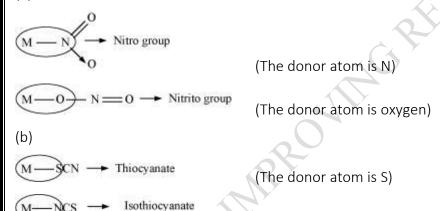
When  $CuSO_4$  and  $NH_3$  are mixed in the molar ratio of 1 : 4 in solution, a complex  $[Cu (NH_3)_4] SO_4$  is formed, which does not dissociates into constituent ions.

#### Ans. 4

Ligands that can attach themselves to the central metal atom through two different atoms are called ambidentate ligands.

#### For example:

(a)



#### Ans 5.

In  $[Co(NH_3)_6]^{3+}$ , cobalt ion is in + 3 oxidation state and has the electronic configuration  $3d^6$ . It undergoes  $d^2sp^3$  hybridisation. Each hybrid orbital receives 1 pair of electrons from ammonia. Since all electrons are paired it is diamagnetic.

(The donor atom is N)

In  $[CoF_6]^{3+}$ , cobalt ion is in + 3 oxidation state and has the electronic configuration  $3d^6$ . It undergoes sp<sup>3</sup> d<sup>2</sup> hybridisation. Each hybrid orbital receives a pair of electrons from F<sup>-</sup>. The 3d electrons of Co remain unpaired making it paramagnetic.

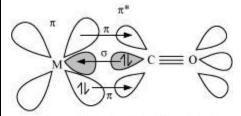
### Ans 6.

Cr is in the +3 oxidation state i.e.,  $d^3$  configuration. Also, NH<sub>3</sub> is a weak field ligand that does not cause the pairing of the electrons in the 3d orbital.

# Downloaded from www.studiestodav.com 244 Cr<sup>3+</sup> Therefore, it undergoes $d^2sp^3$ hybridization and the electrons in the 3d orbitals remain unpaired. Hence, it is paramagnetic in nature. In $[Ni(CN)_4]^{2-}$ , Ni exists in the +2 oxidation state i.e., $d^8$ configuration. Ni<sup>2+:</sup> $CN^-$ is a strong field ligand. It causes the pairing of the 3d orbital electrons. Then, $Ni^{2+}$ undergoes $dsp^2$ hybridization. 11/11/11/11 As there are no unpaired electrons, it is diamagnetic. Ans 7 The splitting of the d orbitals in an octahedral field takes palce in such a way that $\frac{d_{x^2-y^2}}{d_{x^2}}$ , $\frac{d_{x^2}}{d_{x^2}}$ experience a rise in energy and form the $e_g$ level, while $d_{xy}$ , $d_{yz}$ and $d_{zx}$ experience a fall in energy and form the $t_{2g}$ level. Energy Barycentre Average energy of the d orbitals in a spherical field Metal Splitting of the d d orbitals orbitals in a $d_{x^2-v^2}, d_{z^2}, d_{xv}, d_{vz}, d_{xz}$ octahedral crystal field Stronger the ligand, more is the splitting. (a) Higher the oxidation state, greater is the magnitude of $\square_0$ . Ans 8. The metal-carbon bonds in metal carbonyls have both $\sigma$ and $\pi$ characters. A $\sigma$ bond is formed when the

The metal-carbon bonds in metal carbonyls have both  $\sigma$  and  $\pi$  characters. A  $\sigma$  bond is formed when the carbonyl carbon donates a lone pair of electrons to the vacant orbital of the metal. A  $\pi$  bond is formed by the donation of a pair of electrons from the filled metal d orbital into the vacant anti-bonding  $\pi^*$  orbital (also known as back bonding of the carbonyl group). The  $\sigma$  bond strengthens the  $\pi$  bond and vice-versa. Thus, a synergic effect is created due to this metal-ligand bonding. This synergic effect strengthens the bond between CO and the metal.

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Synergic bonding in metal carbonyls

#### Ans 9.

When ionization isomers are dissolved in water, they ionize to give different ions. These ions then react differently with different reagents to give different products.

 $[Co(NH_3)_5Cl]SO_4 + Ba^{2+}$ 

BaSO<sub>4</sub> white precipitate

 $[Co(NH_3)_5Cl]SO_4 + Ag^+$ 

No Reaction

[Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>]CI + Ag<sup>+</sup>

AgCl white precipitate

 $[Co(NH_3)_5SO_4]CI + Ba^{2+}$ 

No Reaction

#### Ans 10

i.  $K_2[Ni(CN)_4]$ 

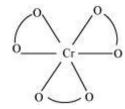
No Isomerism shown by it

ii.  $[Cr(en)_3]Cl_3$ 

Optical isomerism

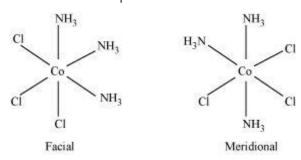
### Answers(three mark questions)

Ans 1. (a) For  $[Cr(C_2O_4)_3]^{3-}$ , no geometric isomer is possible as it is a bidentate ligand.



(b)  $[Co(NH_3)_3Cl_3]$ 

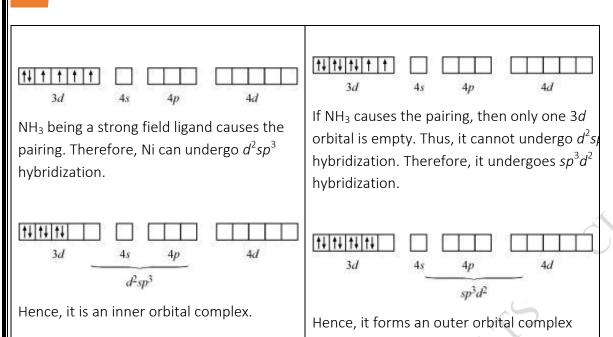
Two geometrical isomers are possible.



Ans 2. (a) hexaaquotitanium(III) ion

(b) Due to presence of single electron in d orbitals so that d-d transition is possible.

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(c) Due to absence of unpaired elect	ron in d orbital		
Ans. 3 (a) Tris-(1,2-ethanediamine) cobalt (II	I) ion		
, , , , , , , , , , , , , , , , , , , ,	) <sub>4</sub> ] are tetrahedral, their magnetic characters a is a weak field ligand and it does not cause the	,	
In Ni(CO)4, Ni is in the zero oxidation state i.	e., it has a configuration of $3d^8 4s^{2}$ .		
3d 4s 4p 4d			
But CO is a strong field ligand. Therefore, it	causes the pairing of unpaired $3d$ electrons. Also giving rise to $sp^3$ hybridization. Since no unpact		
(c) It is because the stability of complex central ion. More is the charge density great	depends upon the charge density (i.e. charg ter is the stability.	e/radius ratio) on	
Ans 4. (a) dsp <sup>2</sup> hybridisation			
(b) Square planer structure			
(c) In $[Ni(H_2O)_6]^{2+}$ , $H_2O$ is a weak field ligand	. Therefore, there are unpaired electrons in Ni <sup>2</sup> n be excited to the higher energy level i.e., ploured.	•	
In [Ni(CN) <sub>4</sub> ] <sup>2-</sup> , the electrons are all paired as possible in [Ni(CN) <sub>4</sub> ] <sup>2-</sup> . Hence, it is colourless	CN <sup>-</sup> is a strong field ligand. Therefore, <i>d-d</i> tran	sition is not	
Ans. 5			
[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	$[Ni(NH_3)_6]^{2+}$		
Oxidation state of cobalt = +3	Oxidation state of Ni = +2		
Electronic configuration of cobalt = $d^6$	Electronic configuration of nickel = $d^8$		
10			
		1	



Ans. 6

complex	Oxidation no. of Ni	hybrid orbitals	shape
(i) [Ni(CN) <sub>4</sub> ] <sup>2-</sup>	+2	dsp <sup>2</sup>	Square planer
(ii) [Ni(Cl) <sub>4</sub> ] <sup>2-</sup>	+2	sp <sup>3</sup>	Tetrahedral
(iii) [Ni(CO) <sub>4</sub> ]	Zero (0)	sp <sup>3</sup>	Tetrahedral

Ans. 7

(a)  $[Co(H_2O)(CN)(en)_2]^{2+}$ oxidation numbers = +3;
coordination number = 6

IUPAC name = aquacynobis-(ethane 1,2diamine) cobalt (III) ion

(b)  $[PtCl_4]^{2-}$ oxidation numbers = +2;
coordination number = 4

IUPAC name = tetachloridoplatinate(II) ion

Ans. 8

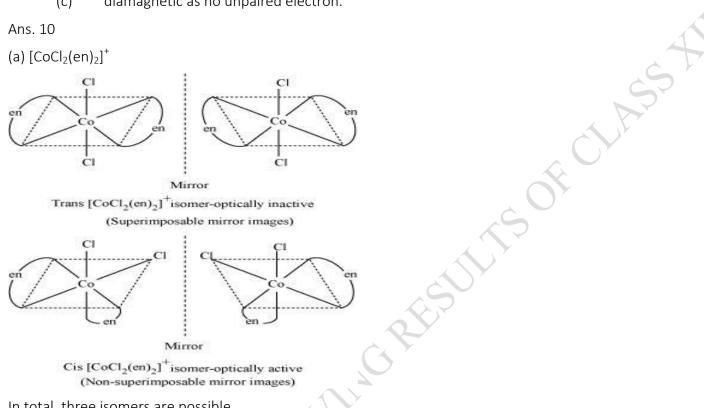
(a)  $[Fe(CN)_6]^{4-}$ In the above coordination complex, iron exists in the +2 oxidation state.  $Fe^{2+}$ : Electronic configuration is  $3d^6$ 

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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
As $CN^-$ is a strong field ligand, it causes the pairing of the unpaired $3d$ electrons.
As Civils a strong field figured, it causes the pairing of the disparred <i>su</i> electrons.
$\frac{1}{3d}$ $\frac{1}{4s}$ $\frac{1}{4p}$
Since there are six ligands around the central metal ion, the most feasible hybridization is $d^2sp^3$ .
$d^2sp^3$ hybridized orbitals of Fe <sup>2+</sup> are:
$d^2sp^3$
6 electron pairs from $CN^-$ ions occupy the six hybrid $d^2sp^3$ orbitals.
6 pairs of electrons
Then, from 6 CN ions
Hence, the geometry of the complex is octahedral and the complex is diamagnetic
(as there are no unpaired electrons).
(b) [FeF <sub>6</sub> ] <sup>3-</sup>
In this complex, the oxidation state of Fe is +3.
Orbitals of Fe <sup>+3</sup> ion:
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
There are 6 F <sup>-</sup> ions. Thus, it will undergo $d^2sp^3$ or $sp^3d^2$ hybridization. As F <sup>-</sup> is a weak field ligand, it does not cause the pairing of the electrons in the 3d orbital. Hence, the most feasible hybridization is $sp^3d^2$ .
$sp^3d^2$ hybridized orbitals of Fe are:
3d $4s$ $4p$ $4d$
$sp^3d^2$
3d $4s$ $4p$ $4d$
sp <sup>3</sup> d <sup>2</sup> 6 electron pairs from F <sup>-</sup> ions
Hence, the geometry of the complex is found to be octahedral.
Ans. 9 (a)

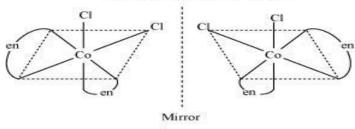
- O. S. = +2(b) bybridisation =  $dsp^2$
- (c) diamagnetic as no unpaired electron.

Ans. 10

(a)  $[CoCl_2(en)_2]^+$ 



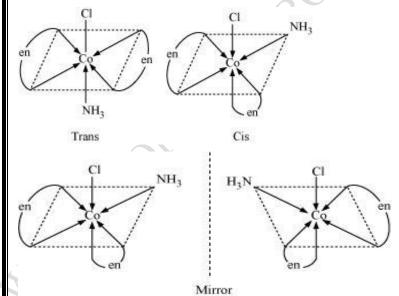
Trans [CoCl2(en)2] isomer-optically inactive (Superimposable mirror images)



Cis [CoCl2(en)2] isomer-optically active (Non-superimposable mirror images)

In total, three isomers are possible.

(b)  $[Co(NH_3)Cl(en)_2]^{2+}$ 



Trans-isomers are optically inactive.

Cis-isomers are optically active

Answers(five mark questions)

#### Ans. 1

- (a) the oxidation No. of Iron = +3
- (b) the hybrid orbitals =  $d^2sp^3$  and the shape of the complex = octahedral
- (c) the magnetic behavior of the complex = Paramagnetic
- (d) No. of geometrical isomers = Two (cis and trans)
- (e) cis structure can show an optical isomer also
- (f) bis-(ethane 1,2diamine)dichloridoplatinum (III) chloride

#### Ans. 2

- (a)  $Co^{2+}$  ion is easily oxidized to  $Co^{3+}$  because  $Co^{3+}$  contains  $t_{2g}^{\phantom{2g}6}$ ,  $e_g^{\phantom{2g}0}$  (stable) electronic configuration in the presence of strong ligand while  $Co^{2+}$  has  $t_{2g}^{\phantom{2g}6}$ ,  $e_g^{\phantom{2g}1}$  (unstable) electronic configuration.
- (b) CO is a stronger complexing reagent than NH<sub>3</sub> due to its capacity to form a synergic (back-bonding or  $d\pi$   $p\pi$  bonding).
- (c) The molecular shape of  $[Ni(CO)_4]$  is not the same as that of  $[Ni(CN)_4]^{2-}$  due to availability of vacant d orbital for the hybridization. [Ni(CO)<sub>4</sub>] is tetrahedral in the structure due to sp<sup>3</sup> hybridization while [Ni(CN)<sub>4</sub>]<sup>2-</sup> is square planer in the structure due to dsp<sup>2</sup> hybridization
- (d) Because of non-availability of inner vacant d-orbital for pairing the electrons.
- (e) due to availability of vacant d- orbitals to form a bond with a ligand.

#### Ans. 3

(i) Potassium diaquadioxalatochromate (III) trihydrate.

Oxidation state of chromium = 3

Electronic configuration:  $3d^3$ :  $t_{2g}$ 

Coordination number = 6

Shape: octahedral

Stereochemistry:

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$$\begin{array}{c|c}
OH_2 & OH_2 \\
OH_2 &$$

Magnetic moment, 
$$\mu = \sqrt{n(n+2)}$$

$$=\sqrt{3(3+2)}$$
$$=\sqrt{15}$$

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Cis is optically active

(ii) [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>

IUPAC name: Pentaamminechloridocobalt(III) chloride

Oxidation state of Co = +3

Coordination number = 6

Shape: octahedral.

Electronic configuration:  $d^6$ :  $t_{2g}^6$ .

Stereochemistry:

Magnetic Moment = 0

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(iii)CrCl<sub>3</sub>(py)<sub>3</sub>

IUPAC name: Trichloridotripyridinechromium (III)

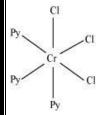
Oxidation state of chromium = +3

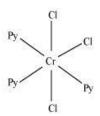
Electronic configuration for  $d^3 = t_{2g}^3$ 

Coordination number = 6

Shape: octahedral.

Stereochemistry:





Facial isomer

Meriodional isomer

Both isomers are optically active. Therefore, a total of 4 isomers exist.

Magnetic moment,  $\mu = \sqrt{n(n+2)}$ 

$$=\sqrt{3\left( 3+2\right) }$$

$$=\sqrt{15}$$
 ~4BM

Ans. 4

(i)

(a)  $[Co(NH_3)_5(NO_2)](NO_3)_2$ 

IUPAC Name: pentaamminenitrocobalt(III) nitrate

It can show two types of isomerism

➤ linkage isomerism.

 $[Co(NH_3)_5(NO_2)](NO_3)_2$  and  $[Co(NH_3)_5(ONO)](NO_3)_2$ 

> ionization isomerism.

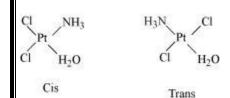
 $[Co(NH_3)_5(NO_2)](NO_3)_2$  and  $[Co(NH_3)_5(NO_3)](NO_3)(NO_2)$ 

(b)[ $Pt(NH_3)(H_2O)Cl_2$ ]

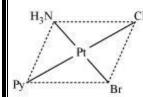
IUPAC Name :ammineaquochloridoplatinum(II)

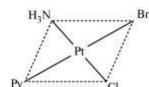
➤ Geometrical (cis-, trans-) isomers of [Pt(NH<sub>3</sub>)(H<sub>2</sub>O)Cl<sub>2</sub>]can exist.

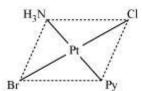




(ii) [Pt(NH<sub>3</sub>)(Br)(Cl)(py)







From the above isomers, none will exhibit optical isomers. Tetrahedral complexes rarely show optical isomerization. They do so only in the presence of unsymmetrical chelating agents.

Ans. 5 (i) In first case, colour will change from blue to deep blue.

$$\left[\text{Cu }(\text{H}_2\text{O})_4\right]^{2^+} + 4 \; \text{NH}_3 \; \rightarrow \; \left[\text{Cu }(\text{NH}_3)_4\right]^{2^+} + 4 \; \text{H}_2\text{O}$$

deep blue

While in second case, its colour will change to yellow.

$$[Cu (H_2O)_4]^{2+} + 4 Cl^- \rightarrow [CuCl_4]^{2+} + 4 H_2O$$

Yellow

- (ii) (a)  $[Cu (NH_3)]_4]^{2+}$  = tetraamminecopper(II)ion
  - (b)  $[CuCl_4]^{2+}$ = tetrachloridocopper(II) ion

Prepared By: Silchar Region

**CHAPTER 9** 

#### COORDINATION COMPOUNDS

1 mark questions

21. Explain coordination entity with example.

Ans: it constitute a central metal atom or ions bonded to a fixed number of molecules or ions ( ligands) .eg.  $[Co(NH_3)_3Cl_3]$ .

22. What do you understand by coordination compounds?

Ans: coordination compounds are the compounds which contains complex ions. These compounds contain a central metal atom or cation which is attached with a fixed number of anions or molecules called ligands through coordinate bonds. eg.  $[Co(NH_3)_3Cl_3]$ 

23. What is coordination number?

Ans: the coordination number of a metal ion in a complex may be defined as the total number of ligand donor atoms to which the metal ion is directly bonded. Eg. In the complex ion  $[Co(NH_3)_6]^{3+}$  has 6 coordination number.

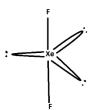
24. Name the different types of isomerisms in coordination compounds.

Ans: structural isomerism and stereoisomerism.

25. Draw the structure of xenon difluoride.

Ans: structure :trigonalbipyramidal

Shape: linear



26. What is spectrochemical series?

Ans: the series in which ligands are arranged in the order of increasing field strength is called spectrochemical series. The order is :

 $I^{-}$ SCN $^{-}$ C $I^{-}$ S $^{2}$ -F $^{-}$ COH $^{-}$ C $_{2}$ O $_{4}$ - $^{2}$ -CH $_{2}$ O<NCS $^{-}$ CEDTA $^{4}$ -CNH $_{3}$ Cen $^{-}$ CO

27. What do you understand by denticity of a ligand?

Ans: the number of coordinating groups present in ligand is called denticity of ligand.

Eg.Bidentateligand ethane-1,2-diamine has 2 donor nitrogen atoms which can link to central metal atom.

28. Why is CO a stronger ligand than Cl<sup>-</sup>?

Ans: because CO has  $\pi$  bonds.

29. Why are low spin tetrahedral complexes not formed?

Ans : because for tetrahedral complexes, the crystal field stabilisation energy is lower than pairing energy.

30. Square planar complexes with coordination number 4 exhibit geometrical isomerism whereas tetrahedral complexes do not. Why?

Ans: tetrahedral complexes do not show geometrical isomerism because the relative positions of the ligands attached to the central metal atom are same with respect to each other.

31. What are crystal fields?

Ans: the ligands has around them negatively charged field because of which they are called crystal fields.

32. What is meant by chelate effect? Give an example.

Ans: when a didentate or polydentate ligand contains donor atoms positioned in such a way that when they coordinate with the central metal atom, a 5 or 6 membered ring is formed, the effect is called chelate effect. Eg.  $[PtCl_2(en)]$ 

33. What do you understand by ambidentate ligand?

Ans: a ligand which contains two donor atoms but only one of them forms a coordinate bond at a time with central metal atom or ion is called an ambidentate ligand. Eg.nitrito-N and nitrito-O.

- 34. What is the difference between homoleptic and heteroleptic complexes?
  - Ans: in homoleptic complexes the central metal atom is bound to only one kind of donor groups whereas in heteroleptic complexes the central metal atom is bound to more than one type of donor atoms.
- 35. Give one limitation for crystal field theory.
  - Ans: i) as the ligands are considered as point charges, the anionic ligands should exert greater splitting effect. However the anionic ligands are found at the low end of the spectrochemical series.
  - ii) it does not take into account the covalent character of metal ligand bond. ( any one )
- 36. How many ions are produced from the complex: [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub>

Ans: 3 ions

37. The oxidation number of cobalt in  $K[Co(CO)_4]$ 

38. Which compound is used to estimate the hardness of water volumetrical

Ans: EDTA

- 39. Magnetic moment of  $[MnCl_4]^{2-}$  is 5.92B.M explain with reason.
  - Ans: the magnetic moment of 5.9 B.M. corresponds to the presence of 5 unpaired electrons in the dorbitals of Mn<sup>2+</sup> ion. As a result the hybridisation involved is sp<sup>3</sup> rather than dsp<sup>2</sup>. Thus tetrahedral structure of [MnCl<sub>4</sub>]<sup>2-</sup> complex will show 5.92 B.M magnetic moment value.
- 40. How many donor atoms are present in EDTA ligand?

Ans: 6

- 11. Give the electronic configuration of the following complexes on the basis of crystal field splitting theory.
  - $[CoF_6]^{3-}$ iv)
  - $[Fe(CN)_{6}]^{4-}$ Ans: i)  $Co^{3+}$  (d<sup>6</sup>)  $t_{2g}^{4}e_{g}^{2}$   $Fe^{2+}$  d<sup>6</sup> $t_{2g}^{6}e_{g}^{0}$
  - vi)
- 12. Explain the following with examples:
  - Linkage isomerism
  - Outer orbital complex
    - Ans: i) this type of isomerism arises due to the presence of ambidentate ligand in a coordination compound. Eg. [Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>]Cl<sub>2</sub> and [Co(NH<sub>3</sub>)<sub>5</sub>ONO]Cl<sub>2</sub>
  - When ns, np and nd orbitals are involved in hybridisation, outer orbital complex is formed. Eg. [CoF<sub>6</sub>]<sup>2-</sup> in which cobalt is sp<sup>3</sup>d<sup>2</sup> hybridised.
- 13. i)Low spin octahedral complexes of nickel are not found . Explain why?
  - ii) the  $\pi$  complexes are known for transition elements only explain.

Ans: i) nickel in its atomic or ionic state cannot afford 2 vacant 3d orbitals and hence d<sup>2</sup>sp<sup>3</sup> hybridisation is not possible.

- ii) transition metals have vacant d orbitals in their atoms or ions into which the electron pairs can be donated by ligands containing  $\pi$ electrons.eg. benzene, ethylene etc. thus  $d\pi$ - $p\pi$  bonding is possible.
- 14. How would you account for the following:
  - iii)  $[Ti(H_2O)_6]^{3+}$  is coloured while  $[Sc(H_2O)_6]^{3+}$  is colourless.
  - iv) [Ni(CO)<sub>4</sub>] possess tetrahedral geometry whereas [Ni(CN)<sub>4</sub>]<sup>2-</sup> is square planar

Ans: i) due to the presence of 1 electron in 3d subshell in  $[Ti(H_2O)_6]^{3+}$  complex d-d transition takes place by the absorption of visible light. Hence the complex appears coloured. On the other hand,  $[Sc(H_2O)_6]^{3+}$  does not possess any unpaired electron .Hence d-d transition is not possible (which is responsible for colour) in this complex is not possible, therefore it is colourless.

- ii) Ni in  $[Ni(CO)_4]$  is sp<sup>3</sup> hybridised. Hence it is tetrahedral. Whereas for  $[Ni(CN)_4]^{2-}$  is  $dsp^2$  hybridised hence it has square planar geometry.
- 15. State reasons for each of the following:
  - iii) All the P—Cl bonds in PCl<sub>5</sub> molecule are not equivalent.
  - iv) S has greater tendency for catenation than O.

Ans: i) in P  $Cl_5$  the 2 axial bonds are longer than 3 equatorial bonds. This is due to the fact that the axial bond pairs suffers more repulsion as compared to equatorial bond pairs.

- ii) The property of catenation depends upon the bond strength of the element. As S—S bond is much stronger (213kJ / mole) than O—O bond (138 kJ/mole), S has greater tendency for catenation than O.
- 16. Give the stereochemistry and the magnetic behaviour of the following complexes:
  - iii)  $[Co(NH_3)_5Cl]Cl_2$
  - iv)  $K_2[Ni(CN)_4]$

Ans: i)  $d^2sp^3$  hybridisation, structure and shape = octahedral Magnetic behaviour- diamagnetic

ii) dsp<sup>2</sup> hybridisation, structure and shape = square planar

magnetic behaviour- diamagnetic

- 17. Draw the structures of isomers if any and write the names of the following complexes:
  - iii)  $\left[ Cr(NH_3)_4 Cl_2 \right]^+$
  - iv)  $[Co(en)_3]^{3+}$

Ans: i) tetraamminedichloridochromium(III) ion

- ii) tris(ethane-1,2-diammine)cobalt(III)ion
- 18. State reasons for each of the following:
  - iv) The N-O bond in NO<sub>2</sub> is shorter than the N-O bond in NO<sub>3</sub>
  - v) SF<sub>6</sub> is kinetically an inert substance.

Ans: i) this is because the N-O bone in  $NO_2^-$  is an average of a single bond and a double bond whereas N-O bond in  $NO_3^-$  is an average of 2 single bonds and a double bond.

- In  $SF_6$  the S atom is sterically protected by 6 fluorine atoms and does not allow water molecules to attack the S atom. Further F atoms does not contain d orbitals to accept the electrons denoted by water molecules. Due to these reasons,  $SF_6$  is kinetically an inert substance
- 19. Hydrated copper sulphate is blue in colour whereas anhydrous copper sulphate is colourless. Why?

Ans: because water molecules act as ligands which splits the d orbital of the  $Cu^{2+}$  metal ion. This result in d-d transition in which  $t_{2g}{}^{6}e_{g}{}^{3}$  excited to  $t_{2g}{}^{5}e_{g}{}^{4}$  and this impart blue colour to the crystal. Whereas when we talk about anhydrous copper sulphate it does not contain any ligand which could split the d orbital to have CFSE effect.

- 20. Calculate the magnetic moment of the metal ions present in the following complexes:
  - iii)  $[Cu(NH_3)_4]SO_4$
  - iv)  $[Ni(CN)_4]^{2-}$

Ans: i)electronicconfig.  $t_{2g}^{6}e_{g}^{3}$ , n=1,  $\mu_{s}$ =  $\forall$ n(n+2) = 1.732 B.M

ii) electronic config.  ${t_{2g}}^6 {e_g}^2$  , n=2,  $\mu_s$  = Vn(n+2)=2.828 B.M

#### 3 marks questions

- 2. (a) What is a ligand? Give an example of a bidentate ligand.
  - (b) explain as to how the 2 complexes of nickel,  $[Ni(CN)_4]^{2^-}$  and  $Ni(CO)_4$  have different structures but donot differ in their magnetic behaviour. (Ni=28)

Ans: (a) the ion, atom or molecule bound to the central atom or ion in the coordination entity is called ligand. A ligand should have lone pair of electrons in their valence orbital which can be donated to central metal atom or ion.

Eg.Bidentate ligand-

ethylenediammine

### H<sub>2</sub>N-H<sub>2</sub>C-CH<sub>2</sub>-NH<sub>2</sub>

(b)dsp<sup>2</sup>, square planar, diamagnetic (n=0)

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Sp<sup>3</sup> hybridisation, tetrahedral geometry, diamagnetic (n=0)

- 2. Nomenclate the following complexes:
- i) [Co(NH<sub>3</sub>)5(CO<sub>3</sub>)]Cl
- ii)[COCl2(en)2]Cl
- iii) Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]

Ans: i) pentaamminecarbonatocobalt(III)chloride

- ii) dichloridobis(ethane-1,2-diamine)cobalt(III)chloride
- iii)iron(III)hexacyanidoferrate(II)
- 3. (a) why do compounds with similar geometry have different magnetic moment?

(b) what is the relationship between the observed colour and wavelength of light absorbed by the complex?

Ans: (a) it is due to the presence of weak and strong ligands in complexes, if CFSE is high the complex will show low value of magnetic moment and if it is low the value of magnetic moment is high. Eg.  $[CoF_6]^{3-}$  and  $[Co(NH_3)_6]^{3+}$ , the former is paramagnetic and the latter is diamagnetic.

- (b) higher the CFS lower will be the wavelength of absorbed light. Colour of the complex is obtained from the wavelength of the leftover light.
- 4. Explain the following terms giving a suitable example.
- (a) ambident ligand
- (b) denticity of a ligand
- (c) crystal field splitting in an octahedral field

Ans (a) Aligand which contains two donor atoms but only one of them forms a coordinate bond at a time with central metal atom or ion is called an ambidentate ligand. Eg.nitrito-N and nitrito-O.

- (b) The number of coordinating groups present in ligand is called denticity of ligand. Eg. Bidentateligand ethane-1,2-diamine has 2 donor nitrogen atoms which can link to central metal atom.
- (c) the splitting of the degenerated d orbital into 3 orbitals of lower energy  $t_2g$  and 2 orbitals of higher energy  $e_g$  due to presence of a ligand in a octahedral crystal field is known as crystal field splitting in an octahedral complex.
- 5. (a) Copper sulphate pentahydrate is blue in colour while anhydrous copper sulphate is colourless. Why?
- (b) Sulphur has greater tendency for catenation than oxygen. Why?

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Ans : (a)because water molecules act as ligands which splits the d orbital of the  $Cu^{2+}$  metal ion. This result in d-d transition in which  $t_{2g}{}^6e_g{}^3$  excited to  $t_{2g}{}^5e_g{}^4$  and this impart blue colour to the crystal. Whereas when we talk about anhydrous copper sulphate it does not contain any ligand which could split the d orbital to have CFSE effect.

- (b)The property of catenation depends upon the bond strength of the element. As S—S bond is much stronger (213kJ / mole) than O—O bond (138 kJ/mole), S has greater tendency for catenation than O.
- 6. draw structures of geometrical isomers of the following complexes:
- (a)  $[Fe(NH_3)_2(CN)_4]^-$  (b)  $[CrCl_2(ox)_2]^{3-}$  (c)  $[Co(en)_3]Cl_3$
- 7. write the state of hybridisation, the shape and the magnetic behaviour of the following complexes:
- (i)  $[Co(en)_3]Cl_3$
- (II)  $K_2[Ni(CN)_4]$
- $(III)[Fe(CN)_6]^{3-}$
- 8. how would you account for the following:
- (i)  $[Ti(H_2O)_6]^{3+}$  is coloured while  $[Sc(H_2O)_6]^{3+}$  is colourless.
- (II)  $[Fe(CN)_6]^{3-}$  is weakly paramagnetic while  $[Fe(CN)_6]^{4-}$  is diamagnetic.
- (III) Ni(CO)<sub>4</sub> possess tetrahedral geometry while [Ni (CN)<sub>4</sub>]<sup>2-</sup> is square planar.

Ansi) due to the presence of 1 electron in 3d subshell in  $[Ti(H_2O)_6]^{3+}$  complex d-d transition takes place by the absorption of visible light. Hence the complex appears coloured. On the other hand,  $[Sc(H_2O)_6]^{3+}$  does not possess any unpaired electron .Hence d-d transition is not possible (which is responsible for colour) in this complex is not possible, therefore it is colourless.

- (ii) paramagnetism is attributed to the presence of unpaired electrons. Greater the number of unpaired electron greater is the paramagnetism. Due to the presence of one electron in the 3d subshell in  $[Fe(CN)_6]^{3-}$  it is weakly paramagnetic. On the other hand  $[Fe(CN)_6]^{4-}$  is diamagnetic because all electrons are paired.
- iii) Ni in  $[Ni(CO)_4]$  is  $sp^3$  hybridised. Hence it is tetrahedral. Whereas for  $[Ni(CN)_4]^{2^-}$  is  $dsp^2$  hybridised hence it has square planar geometry.
  - 11. Explain the following ::
    - (iv) low spin octahedral complexes of Ni are not known.
    - (v) The pi complexes are known for the transition elements only.
    - (vi) CO is a stronger ligand than NH<sub>3</sub> for many metals

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Ans. i) nickel in its atomic or ionic state cannot afford 2 vacant 3d orbitals and hence  $d^2sp^3$  hybridisation is not possible.

- ii) transition metals have vacant d orbitals in their atoms or ions into which the electron pairs can be donated by ligands containing  $\pi$ electrons.eg. benzene, ethylene etc. thus  $d\pi$ - $p\pi$  bonding is possible.
- (iii) because in case of CO back bonding takes place in which the central atom uses its filled d orbitals with empty anti bonding  $\pi^*$  molecular orbital of CO.
  - 12. What is meant by stability of a coordination compounds in solutions? State the factors which govern the stability of complexes.

Ans: the stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the equilibrium constant for the association expresses the stability.

$$M + 4 L \longrightarrow ML_4$$
  
 $K = [ML_4]/[M][L]^4$ 

Factors on which stability of complex depends (i) charge on central metal ion (ii) nature of the metal ion (iii) basic nature of the ligand (iv) presence of the chelate ring (v) effect of multidentate cyclic ligand .

### 5 marks questions

- 6. Draw the structures of the following molecules:
- (a)  $[Fe(NH_3)_2(CN)_4]^{-}$  (b)  $[CrCl_2(ox)_2]^{3-}$  (c)  $[Co(en)_3]Cl_3(d)$   $[Co(en)_3]Cl_3(e)$   $[Fe(CN)_6]^{3-}$ 
  - 7. What is crystal field theory for octahedral complexes? Also write the limitations of this theory. Ans:
  - 8. Write the state of hybridisation the shape and the magnetic behaviour of the following complex entities:
    - (vi)  $[Cr(NH_3)_4Cl_2]Cl$
    - (vii) [Co(en)<sub>3</sub>]Cl<sub>3</sub>
    - (viii) K<sub>2</sub>[NiCl<sub>4</sub>]
    - (ix)  $[Fe(H_2O)_6]^{2+}$
    - (x)  $[NiCl_4]^{2-}$
  - 9. Using valence bond theory explain the following questions in relation to  $[Co(NH_3)_6]^{3+}$ .
    - (vi) Nomenclature
    - (vii) Type of hybridisation
    - (viii) Inner or outer orbital complex
    - (ix) Magnetic behaviour
    - (x) Spin only magnetic moment

10. Compare the following complexes with respect to structural shape of units, magnetic behaviour and hybrid orbitals involved in units: $ \left[ \text{Co(NH}_3)_6 \right]^{3+}, \left[ \text{Cr(NH}_3)_6 \right]^{3+}, \left[ \text{Ni(CO)}_4 \right] $