

1. Write the IUPAC names for the following complex

- $\text{Na}_2[\text{Ni}(\text{EDTA})]$ – Sodium 2,2', 2'', 2'''– (ethane diylidinitrilo)tetraacetatonickelate(II)
- $[\text{Ag}(\text{CN})_2]^-$ - Dicyanidoargentate(I)ion
- $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$ - Tris(ethane 1, 2 – diamine)cobalt(III)sulphate
- $[\text{Co}(\text{ONO})(\text{NH}_3)_5]^{2+}$ - Pentaamminenitrito-K –O- cobalt(III)ion
- $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO})_2]$ - Diamminechloridonitro-K– N platinum (II)

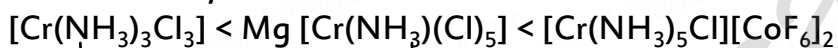
2. Write the formula for the following coordination compounds.

- potassiumhexacyanidoferrate(II) - $\text{K}_4[\text{Fe}(\text{CN})_6]$
- pentacarbonyliron(0) - $[\text{Fe}(\text{CO})_5]$
- pentaamminenitrito – _ –N-cobalt(III)ion - $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$
- hexaamminecobalt(III)sulphate – $[\text{Co}(\text{NH}_3)_6](\text{SO}_4)_3$
- sodiumtetrafluoridodihydroxidochromate(III) - $\text{Na}_3[\text{CrF}_4(\text{OH})_2]$

3. Arrange the following in order of increasing molar conductivity

- $\text{Mg} [\text{Cr}(\text{NH}_3)(\text{Cl})_5]$ ii) $[\text{Cr}(\text{NH}_3)_5\text{Cl}][\text{CoF}_6]_2$ iii) $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3] <$

Molar conductivity increases as the number of ions increases.

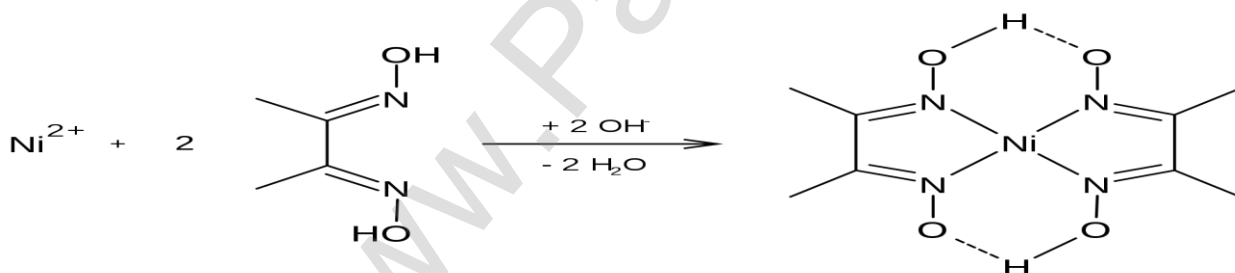


↓
0 ions

↓
2 ions

↓
5 ions

4. Ni^{2+} is identified using alcoholic solution of dimethyl glyoxime. Write the structural formula for the rosy red precipitate of a complex formed in the reaction.

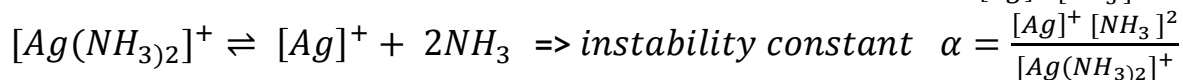
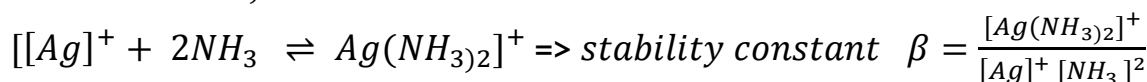


- ❖ The Ni^{2+} reacts with two dimethylglyoxime molecules acting as **chelating agents** to form rosy red color neutral complex known as bis(dimethyl glyoxime)nickel(II).
- ❖ This reaction is used as a confirmation test for the presence of nickel(II) cations.

5. $[\text{CuCl}_4]^{2-}$ exists while $[\text{CuI}_4]^{2-}$ does not exist why?

- ❖ In $[\text{CuI}_4]^{2-}$ complex the size of the chlorine atoms is less so it exists. But in $[\text{CuCl}_4]^{2-}$ the bigger atom makes the compound unstable.
- ❖ Cu^{2+} is reduced to Cu^+ by I^- , hence cupric iodide is converted into cuprous iodide so $[\text{CuI}_4]^{2-}$ does not exist, Cl^- cannot effect this change and thus $[\text{CuCl}_4]^{2-}$ exists.

6. Calculate the ratio of in $\frac{[Ag]}{[Ag(NH_3)_2]^+}$ 0.2 M solution of NH_3 . If the stability constant for the complex $[Ag(NH_3)_2]^+$ is 1.7×10^7



$$\beta = \frac{1}{\alpha} ; \beta = 1.7 \times 10^7 ; \alpha = ? \Rightarrow \alpha = \frac{1}{\beta} = \frac{1}{1.7 \times 10^7}$$


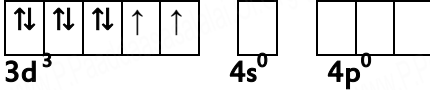
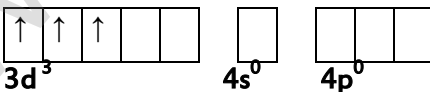
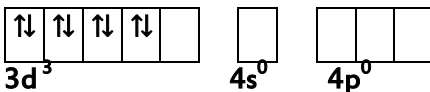
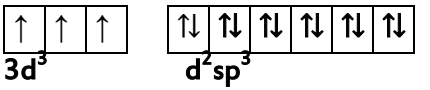
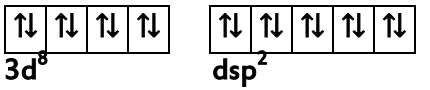
$$\alpha = \frac{1}{1.7 \times 10^7} = 5.88 \times 10^{-8}$$

7. Give an example of coordination compound used in medicine and two examples of biologically important coordination compounds.

Many complexes are used as medicines for the treatment of various diseases. For example,

- ❖ Ca-EDTA chelate, is used in the treatment of lead and radioactive poisoning. That is for removing lead and radioactive metal ions from the body.
- ❖ Cis-platin is used as an antitumor drug in cancer treatment.
 - i) Haemoglobin - for oxygen carrier in blood.
 - ii) Chlorophyll - for photosynthesis in plant.

8. Based on VB theory explain why $[Cr(NH_3)_6]^{3+}$ is paramagnetic, while $[Ni(CN)_4]^{2-}$ is diamagnetic.

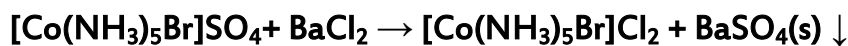
	Complex	$[Cr(NH_3)_6]^{3+}$	$[Ni(CN)_4]^{2-}$
1	Central metal ion and its outer configuration	$Cr^{3+} 3d^3 4s^0$	$Ni^{2+} 3d^8 4s^0$
2	Outer orbital of metal ion		
3	Nature of the ligand	NH_3 Weak field ligand Does not pair up 3d orbital	CN^- Strong field ligand Pair up 3d orbital
4	Outer orbitals in the presence of ligand		
5	Hybridization	Co. no -6 Hybridization - d^2sp^3	Co. no -4 Hybridization - d^2sp^2
6	Hybridized orbitals of the metal atom in the complex		
7	Geometry	Octahedral	Square planar
8	Orbital complex	Inner orbital	Inner orbital
9	Magnetic property	No. of unpaired electrons = 3 Paramagnetic	No. of unpaired electrons = 0 Diamagnetic
	Magnetic moment	$\mu_s \sqrt{n(n+2)}$ $\sqrt{3(3+2)} = 3.87 \text{ MB}$	$\mu_s \sqrt{n(n+2)} = 0$

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ions then react differently with different reagents to give different products.

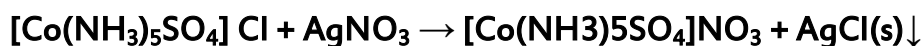
❖ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ are ionization isomers.

i) When $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ reacts with Barium chloride solution it gives white precipitate of BaSO_4



But $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ complex does not answer this test

ii) When $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ reacts with Silver nitrate solution gives white precipitate of silver chloride is formed.



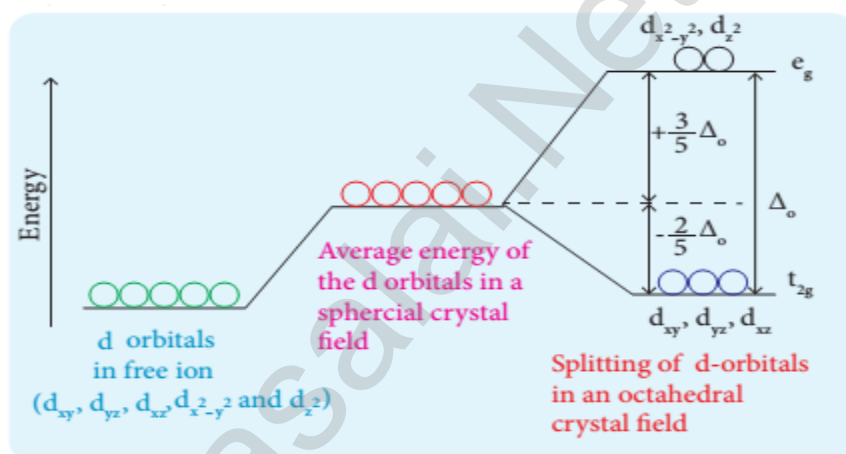
13. In an octahedral crystal field, draw the figure to show splitting of d orbitals.

❖ In an octahedral complex, the metal ion is at the centre and the ligands are at the six corners.

❖ The directions x, y and z point to the three adjacent corners of the octahedron.

❖ The lobes of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) point along the x, y and z axis

❖ While the lobes of the t_{2g} orbitals (d_{xy} , d_{zx} and d_{yz}) point in between the axes.



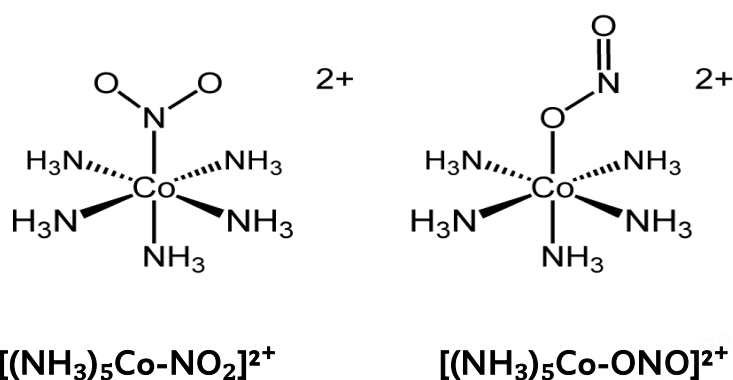
❖ As a result, the approach of six ligands along the x, y z, -x, -y and -z directions will increase the energy of $d_{x^2-y^2}$ and d_{z^2} orbitals (which point towards the ligands)

❖ It increases the energy of d_{xy} , d_{zx} and d_{yz} orbitals (which point in between the metal-ligand bond axis).

14. What is linkage isomerism? Explain with an example.

❖ This type of isomers arises when an ambidentate ligand is bonded to the central metal atom/ion through either of its two different donor atoms.

❖ For example, the nitrite ion is bound to the central metal ion Co^{3+} through a nitrogen atom in one complex, and through oxygen atom in other complex.



15. Write briefly about the applications of coordination compounds in volumetric analysis.

The coordination compounds used for various purposes, in volumetric analysis

❖ **Colour Tests:** Since many complexes are highly coloured they can be used as colour metric reagents e.g. formation of red 2,2'-bipyridyl and 1,10-phenanthroline complexes as a test for Fe^{2+}

❖ **Gravimetric Analysis:** Here chelating ligands are often used to form insoluble complexes e.g. $\text{Ni}(\text{DMG})_2$ and $\text{Al}(\text{oxine})_3$.

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

16. Classify the following ligand based on the number of donor atoms.

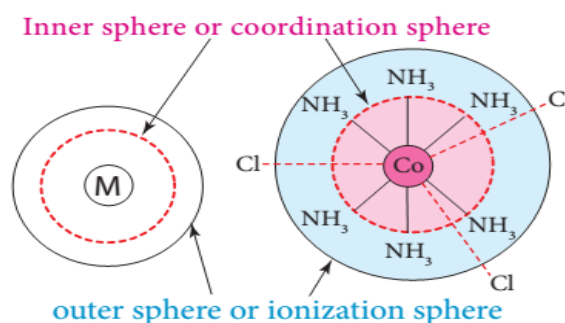
S.no	Ligand	Type of Ligand
1.	NH_3	Monodentate Ligand
2.	en-	Bidentate Ligand
3.	ox^{2-}	Bidentate Ligand
4.	Triamino triethylamine	Tridentate Ligand
5.	Pyridine	Monodentate ligand

17. Give the difference between double salts and coordination compounds.

	Double salt	Coordination compounds.
1.	The compound prepared by combination of two different salts	The compound composed of a central metal ion having coordination bond with ligands
2.	contain ionic bonds between cations and anions.	contain coordinate covalent bonds between metal ion and ligands.
3.	When dissolved in water, double salts are dissociated into ionic species.	They are soluble compounds and are not separated into ionic species.
4.	Can be easily analyzed by determining the ions present in the aqueous solution.	Cannot be easily analyzed by determining the ions present in the aqueous solution
5.	$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ –Mohr's salt	$K_3[Fe(SCN)_6]$

18. Write the postulates of Werner's theory.

- ❖ The central metal or the metal atoms in coordination compounds show two types of valency. They are the primary and secondary valency.
- ❖ The primary valency relates to the oxidation state and the secondary valency relates to the coordinate number.
- ❖ Primary valencies are ionizable and are satisfied by the negative ions.
- ❖ Secondary valencies are non-ionizable. These are satisfied by negative ions. Also, the secondary valence is fixed for any metal and is equal to its coordination number.
- ❖ According to Werner, there are two spheres of attraction around a metal atom/ion in a complex.
- ❖ The inner sphere is known as coordination sphere and the groups present in this sphere are firmly attached to the metal. The outer sphere is called ionisation sphere.



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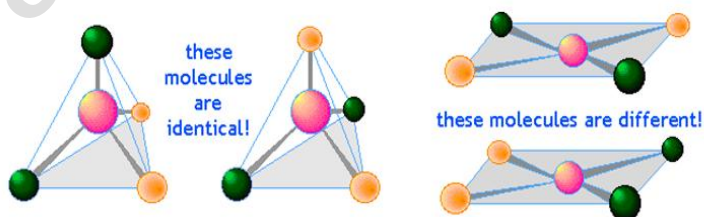
- ❖ The groups present in this sphere are loosely bound to the central metal ion and hence can be separated into ions upon dissolving the complex in a suitable solvent.

19. $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic, while $[\text{NiCl}_4]^{2-}$ is paramagnetic, explain using crystal field theory.

	$[\text{Ni}(\text{CN})_4]^{2-}$	$[\text{NiCl}_4]^{2-}$
Electronic configuration of Ni atom in ground state	$3d^8 \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \quad 4s^2 \uparrow\downarrow \quad 4p^0$	$3d^8 \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \quad 4s^2 \uparrow\downarrow \quad 4p^0$
Ni^{2+} ion	$3d^8 \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \quad 4s^0 \quad 4p^0$	$3d^8 \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \quad 4s^0 \quad 4p^0$
Nature of Ligand	CN^- - strong field ligand	Cl^- weak field ligand
Electronic configuration of Ni atom in the complexes	$3d^8 \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \quad 4d^2 \uparrow\downarrow \uparrow\downarrow$ <div style="text-align: center;"> $\uparrow \quad \uparrow \quad \uparrow \quad \uparrow$ $\text{CN}^- \quad \text{CN}^- \quad \text{CN}^- \quad \text{CN}^-$ </div>	$3d^8 \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \quad 4d^2 \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$ <div style="text-align: center;"> $\uparrow \quad \uparrow \quad \uparrow \quad \uparrow$ $\text{Cl}^- \quad \text{Cl}^- \quad \text{Cl}^- \quad \text{Cl}^-$ </div>
Hybridisation	dsp^2	sp^3
Geometry	Square planar	Tetrahedral
Magnetic property	No unpaired electrons Diamagnetic	Two unpaired electrons Paramagnetic

20. Why tetrahedral complexes do not exhibit geometrical isomerism.

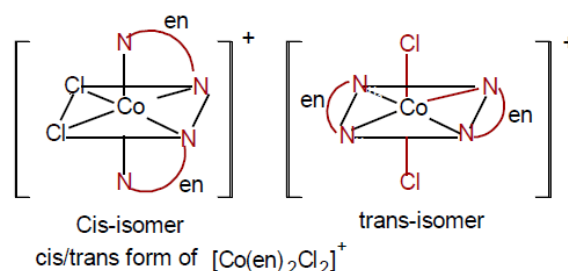
- ❖ Because all the four ligands are **adjacent or equidistant** to one another in tetrahedral complex.
- ❖ The relative positions of donor atoms of ligands attached to the central atom are same with respect to each other.



21. Explain optical isomerism in coordination compounds with an example.

The complexes which are non-superimposable on their mirror images are optically active.

- ❖ Optically active complexes are asymmetric in nature i.e. not divisible into two identical halves. Levorotatory (l) – the compound which rotates plane polarised light to left hand side.
- ❖ Dextrorotatory (d) – the compound which rotates plane polarised light to right hand side
- ❖ d and l isomers of a compound are called enantiomers.



- ❖ Octahedral complexes with coordination number 6 involving 2 or 3 bidentate ligands show optical isomerism.

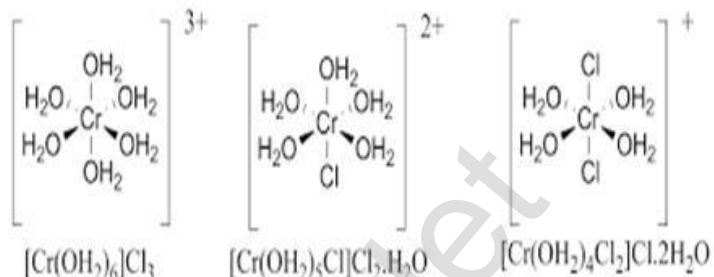
22. What are hydrate isomers? Explain with an example.

- ❖ The exchange of free solvent molecules such as water, ammonia, alcohol etc. in the crystal lattice with a ligand in the coordination entity will give solvate isomers.
- ❖ If the solvent molecule is water, then these isomers are called hydrate isomers.
- ❖ The best known example of this occurs for chromium chloride " $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ " which may contain 4, 5, or 6 coordinated water molecules.

- ❖ $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ - Violet

- ❖ $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ - Pale green

- ❖ $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ - Dark-green



- ❖ 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.

23. What is crystal field splitting energy?

- ❖ The degenerate d-orbitals split into two levels i.e., e_g and t_{2g} in the presence of ligands.
- ❖ The splitting of the degenerate levels due to the presence of ligands is called the crystal-field splitting energy.
- ❖ While the energy difference between the two levels (e_g and t_{2g}) is called the crystal-field splitting energy.
- ❖ It is denoted by Δ_o .

24. What is crystal field stabilization energy (CFSE) ?

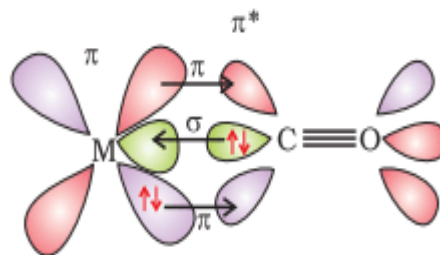
- ❖ The crystal field stabilisation energy is defined as the energy difference of electronic configurations in the ligand field (E_{LF}) and the isotropic field/barycentre (Eiso).
- ❖ $\text{CFSE} (\Delta E_o) = \{E_{LF}\} - \{\text{Eiso}\} = \{[n_{t_{2g}} (-0.4) + n_{e_g} (0.6)] \Delta_o + n_p P\} - \{n'_p P\}$
- ❖ Where $n_{t_{2g}}$ is the number of electrons in t_{2g} orbitals;
- ❖ n_{e_g} is number of electrons in e_g orbitals;
- ❖ n_p is number of electron pairs in the ligand field
- ❖ n'_p is the number of electron pairs in the isotropic field (barycentre).

25. A solution of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green, whereas a solution of $[\text{Ni}(\text{CN})_4]^{2-}$ is colourless. Explain.

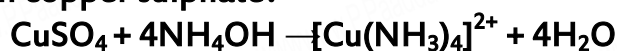
- ❖ $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ consists of Ni^{+2} ion with $3d^8$ electronic configuration.
- ❖ In this configuration, there are two unpaired electrons which cannot pair up because H_2O is a weak ligand.
- ❖ Thus, the d-d transition absorbs the incoming light and it emits a green light.
- ❖ Thereby, giving a green color to the solution.
- ❖ $[\text{Ni}(\text{CN})_4]^{2-}$ consists of Ni^{+2} ion with $3d^8$ electronic configuration.
- ❖ But, CN^- is present here, which is a strong ligand and in its presence, the unpaired electrons pair up.
- ❖ Thus, there is no d-d transition so no color.

26. Discuss briefly the nature of bonding in metal carbonyls. www.Padasalai.Net www.TrbTnpsc.com

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



27. What is the coordination entity formed when excess of liquid ammonia is added to an aqueous solution copper sulphate?



Tetraamminecopper(II)sulphate

CuSO_4 reacts with excess liquid ammonia gives deep blue complex called Tetraamminecopper(II)sulphate. Coordination entity is $[\text{Cu}(\text{NH}_3)_4]^{2+}$

28. On the basis of VB theory explain the nature of bonding in $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$

	Complex	$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$
1	Central metal ion and its outer configuration	$\text{Co}^{3+} 3d^6 4s^0$
2	Outer orbital of metal ion	
3	Nature of the ligand	$(\text{C}_2\text{O}_4)_3^{2-}$ Weak field Ligand and hence no pairing of 3d orbital
4	Outer orbitals in the presence of ligand	
5	Hybridization	Co. no -6 Hybridization – $sp^3 d^2$
6	Hybridized orbitals of the metal atom in the complex	
7	Geometry	Octahedral
8	Orbital complex	Outer orbital complex
9	Magnetic property	No. of unpaired electrons = 4 Paramagnetic
	Magnetic moment	= 4.899 BM

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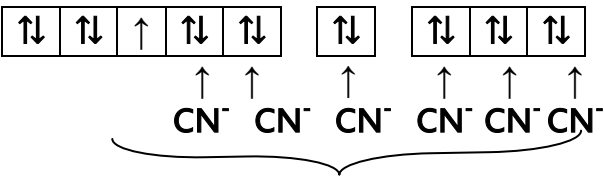
29. What are the limitations of VB theory?

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1. It does not explain the colour of the complex
2. It considers only the spin only magnetic moments and does not consider the other components of magnetic moments.
3. It does not provide a quantitative explanation as to why certain complexes are inner orbital complexes and the others are outer orbital complexes for the same metal.

For example, $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic (low spin) whereas $[\text{FeF}_6]^{4-}$ is paramagnetic (high spin)

30. Write the oxidation state, coordination number, nature of ligand, magnetic property and electronic configuration in octahedral crystal field for the complex $\text{K}_4[\text{Mn}(\text{CN})_6]$

Complex	$\text{K}_4[\text{Mn}(\text{CN})_6]$
1. Electronic configuration in isotropic field	d^5  no. of paired electrons (n_p) = 0 $E_{\text{iso}} = 0$
2. Oxidation state and coordination no	Mn is +2 ; Coordination no : 6
3. Nature of Ligand	CN^- is a strong field Ligand
4. Ligand field	$\text{CFSE} (\Delta E_o) = \text{CFSE} (\Delta E_o) = \{E_{\text{LF}}\} - \{E_{\text{iso}}\}$ $= \{[5(-0.4) + 0(0.6)] \Delta_o + 2P\} - \{0P\}$ $= -2 \Delta_o + 2P = (-2 \times 35000) + (2 \times 30000)$ $= -10000 \text{ cm}^{-1}$ Negative CFSE value indicates that low spin complex is favourable
5. Nature of the complex	Low spin complex
6. Electronic configuration in octahedral field of $\text{K}_4[\text{Mn}(\text{CN})_6]$ $t_2g^5 e_g^0$	 d^2sp^3 hybridisation
7. Magnetic property	No. of unpaired electrons = 1 Paramagnetic
8. Magnetic moment (using low spin)	$\mu_s \sqrt{n(n+2)} = \sqrt{1(1+2)}$ $= 1.732 \text{ BM}$

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