Coordination Compounds JEE Main PYQ - 3

Total Time: 1 Hour : 15 Minute **Total Marks:** 120

Instructions

Instructions

1. Test will auto submit when the Time is up.
2. The Test comprises of multiple choice questions (MCQ) with one or more correct answers.
3. The clock in the top right corner will display the remaining time available for you to complete the examination.

Navigating & Answering a Question

1. The answer will be saved automatically upon clicking on an option amongst the given choices of answer.
2. To deselect your chosen answer, click on the clear response button.
3. The marking scheme will be displayed for each question on the top right corner of the test window.

Coordination Compounds

1. The secondary valency and the number of hydrogen bonded water molecule(s) in $CuSO_4 \cdot 5H_2O$, respectively, are : (+4, -1)

   a. 4 and 1

   b. 6 and 4

   c. 5 and 1

   d. 6 and 5

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2. The stepwise formation of $[Cu(NH_3)_4]^{2+}$ is given. The value of stability constants K_1, K_2, K_3 and K_4 are $10^4, 1.58 \times 10^3, 5 \times 10^2$ and 10^2 respectively. The overall equilibrium constant for dissociation of $[Cu(NH_3)_4]^{2+}$ is $x \times 10^{-12}$. The value of x is ___________. (Rounded off to the nearest integer) (+4, -1)

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3. The hybridization and magnetic nature of $[Mn(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$, respectively are : (+4, -1)

   a. d^2sp^3 and paramagnetic

   b. sp^3d^2 and diamagnetic

   c. d^2sp^3 and diamagnetic

   d. sp^3d^2 and paramagnetic

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4. The number of geometrical isomers possible in triamminetrinitrocobalt(III) is X and in trioxalatochromate(III) is Y. Then the value of X+Y is __________. (+4, -1)

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5. The number of geometrical isomers found in the metal complexes $[PtCl_2(NH_3)_2]$, $[Ni(CO)_4]$, $[Ru(H_2O)_3Cl_3]$ and $[CoCl_2(NH_3)_4]^+$ respectively, are : (+4, -1)

   a. 1, 1, 1, 1

   b. 2, 0, 2, 2

   c. 2, 1, 2, 1

d. 2, 1, 2, 2

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6. **The type of hybridisation and magnetic property of the complex $[MnCl_6]^{3-}$, respectively, are :** **(+4, -1)**

a. d^2sp^3 and paramagnetic

b. sp^3d^2 and diamagnetic

c. sp^3d^2 and paramagnetic

d. d^2sp^3 and diamagnetic

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7. **Given below are two statements:** **(+4, -1)**
Statement I: The identification of Ni^{2+} is carried out by dimethyl glyoxime in the presence of NH_4OH.
Statement II: The dimethyl glyoxime is a bidentate neutral ligand.

a. Both Statement I and Statement II are true.

b. Both Statement I and Statement II are false.

c. Statement I is true but Statement II is false.

d. Statement I is false but Statement II is true.

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8. **In which of the following order the given complex ions are arranged correctly with respect to their decreasing spin only magnetic moment?** **(+4, -1)**
(i) $[FeF_6]^{3-}$ (ii) $[Co(NH_3)_6]^{3+}$ (iii) $[NiCl_4]^{2-}$ (iv) $[Cu(NH_3)_4]^{2+}$

a. (i)>(iii)>(iv)>(ii)

b. (ii)>(iii)>(i)>(iv)

c. (iii)>(iv)>(ii)>(i)

d. (ii)>(i)>(iii)>(iv)

9. Spin only magnetic moment in BM of $[\mathrm{Fe(CO)_4(C_2O_4)}]^+$ is : (+4, -1)

a. 1

b. 1.73

c. 5.92

d. 0

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10. The denticity of an organic ligand, biuret is : (+4, -1)

a. 2

b. 4

c. 6

d. 3

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11. The number of optical isomers possible for $[\mathrm{Cr(C_2O_4)_3}]^{3-}$ is __________. (+4, -1)

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12. The number of moles of CuO, that will be utilized in Dumas method for estimating nitrogen in a sample of 57.5 g of N,N-dimethylaminopentane is $x \times 10^{-2}$. (Nearest integer) (+4, -1)

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13. 1 mol of an octahedral metal complex with formula $MCl_3 \cdot 2L$ on reaction with excess of $AgNO_3$ gives 1 mol of $AgCl$. The denticity of Ligand L is __________. (Integer answer) (+4, -1)

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14. The number of moles of NH_3 that must be added to 2 L of 0.80 M $AgNO_3$ in order to reduce the concentration of Ag^+ ions to 5.0×10^{-8} M ($K_{\text{formation}}$ for $[Ag(NH_3)_2]^+ = 1.0 \times 10^8$) is __________. (Nearest integer) [Assume no volume change on adding NH_3] (+4, -1)

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15. Acidic ferric chloride solution on treatment with excess of potassium ferrocyanide gives a Prussian blue coloured colloidal species. It is: (+4, -1)

a. $Fe_4[Fe(CN)_6]_3$

b. $HFe[Fe(CN)_6]$

c. $KFe[Fe(CN)_6]$

d. $K_2Fe[Fe(CN)_6]_2$

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16. The ratio of number of water molecules in Mohr's salt and potash alum is __________ $\times 10^{-1}$. (Integer answer) (+4, -1)

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17. Which one of the following complexes is violet in colour ? (+4, -1)

a. $[Fe(SCN)_6]^{3-}$

b. $[Fe(CN)_5NOS]^{4-}$

c. $Fe_4[Fe(CN)_6]_3 \cdot H_2O$

d. $[Fe(CN)_6]^{4-}$

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18. The overall stability constant of the complex ion $[\mathrm{Cu(NH_3)_4}]^{2+}$ is 2.1 $\times$ 10^{13}. The overall dissociation constant is y$\times 10^{-14}$. Then y is ___________. (Nearest integer) (+4, -1)

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19. Indicate the complex/complex ion which did not show any geometrical isomerism : (+4, -1)

a. $[\mathrm{CoCl_2(en)_2}]$

b. $[\mathrm{Co(CN)_5(NC)}]^{3-}$

c. $[\mathrm{Co(NH_3)_4Cl_2}]^{+}$

d. $[\mathrm{Co(NH_3)_3(NO_2)_3}]$

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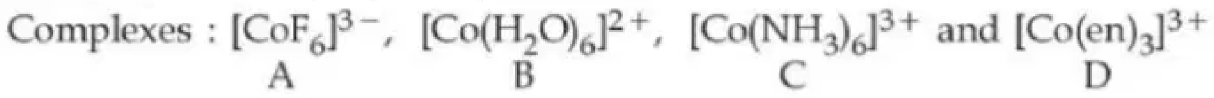
20. Arrange the following Cobalt complexes in the order of increasing Crystal Field Stabilization Energy (CFSE) value. (+4, -1)



Complexes : $\underset{A}{[\mathrm{CoF_6}]^{3-}}$, $\underset{B}{[\mathrm{Co(H_2O)_6}]^{2+}}$, $\underset{C}{[\mathrm{Co(NH_3)_6}]^{3+}}$ and $\underset{D}{[\mathrm{Co(en)_3}]^{3+}}$

a. A < B < C < D

b. B < C < D < A

c. C < D < B < A

d. B < A < C < D

---

21. The number of paramagnetic complexes among $[FeF_6]^{3-}$, $[Fe(CN)_6]^{3-}$, $[Mn(CN)_6]^{3-}$, $[Co(C_2O_4)_3]^{3-}$, $[MnCl_6]^{3-}$ and $[CoF_6]^{3-}$, which involved d^2sp^3 hybridization is .... (+4, -1)

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22. An octahedral complex having molecular composition Co.5NH$_3$.Cl.SO$_4$ has two isomers A and B. The solution of A gives a white precipitate with AgNO$_3$ solution and the solution of B gives a white precipitate with BaCl$_2$ solution. The type of isomerism exhibited by the complex is, **(+4, -1)**

a. Co-ordinate isomerism

b. Linkage isomerism

c. Ionisation isomerism

d. Geometrical isomerism

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23. The ratio of spin-only magnetic moment values $\mu_{\text{eff}}[Cr(CN)_6]^{3-}/\mu_{\text{eff}}[Cr(H_2O)_6]^{3+}$ **is_____** **(+4, -1)**

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24. The complex that dissolves in water is: **(+4, -1)**

a. $Fe_4[Fe(CN)_6]_3$, Prussian Blue insoluble

b. $Fe_6[Fe(CN)_6]_3$

c. $K_4[Co(CO)_6]$

d. $(NH_4)_6[As(MoO_4)_6]$

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25. The set which does not have ambidentate ligands (labeled as (i)) is: **(+4, -1)**

a. CO_3^{2-}, NO_3^-, NCS^-

b. $EDTA^-$, NCS^-, CO_2^{2-}

c. NO^-, CO_3^{2-}, $EDTA^-$

d. CO_2^{2-}, ethylene diamine, H_2O

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26. Which of the following complex has a possibility to exist as meridional isomer? **(+4, -1)**

a. $[Co(en)_3]Cl_3$

b. $[Pt(NH_3)_2]Cl_2$

c. $[Co(en)_3]$

d. $[Co(NH_3)_3(NO_3)_3]$

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27. Formation of which complex, among the following, is not a confirmatory test of Pb^{2+} ions **(+4, -1)**

a. lead sulphate

b. lead nitrate

c. lead chromate

d. lead iodide

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28. The steam volatile compounds among the following are: **(+4, -1)**

(A)

(B)

(C)

(D)

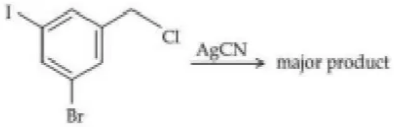
a. (A) and (B) Only

b. (A),(B) and (C) Only

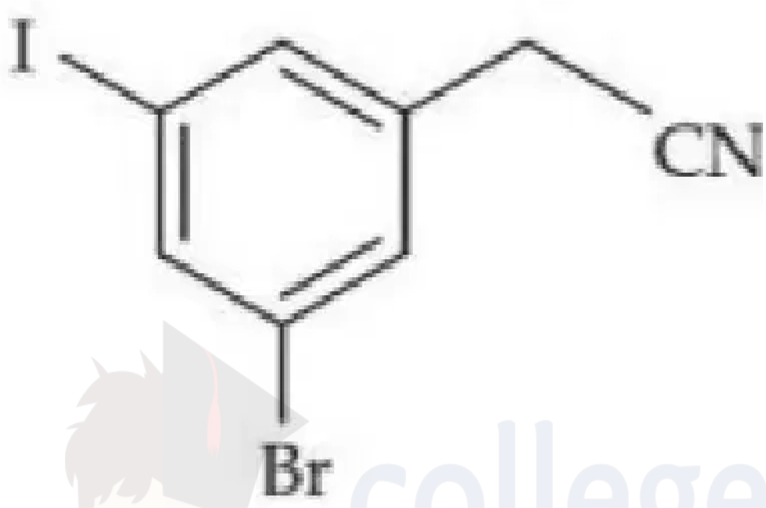
c. (B) and (D) Only

d. (A) and (C) Only

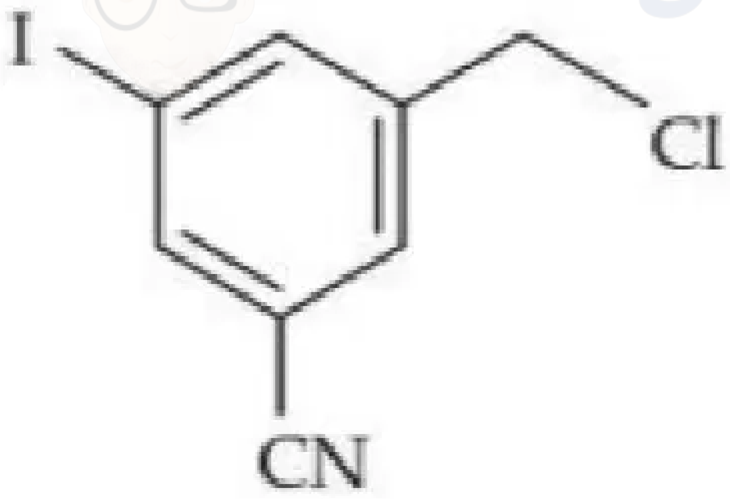
29. The structure of the major product formed in the following reaction is: (+4, -1)

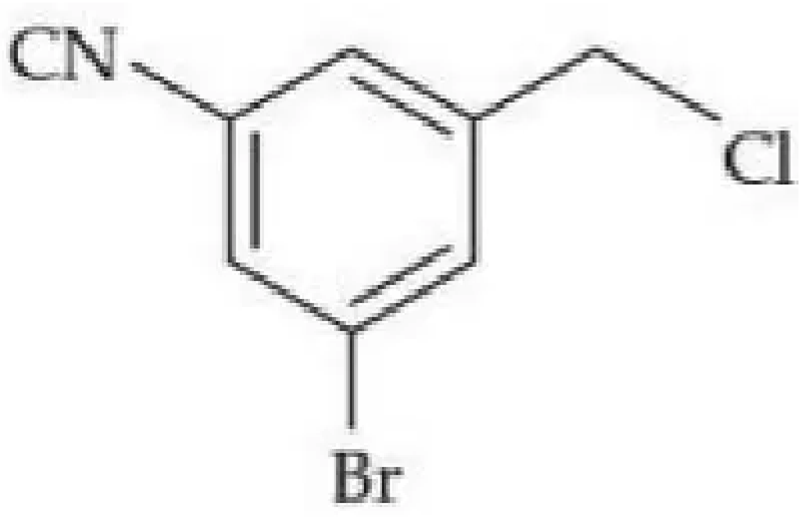


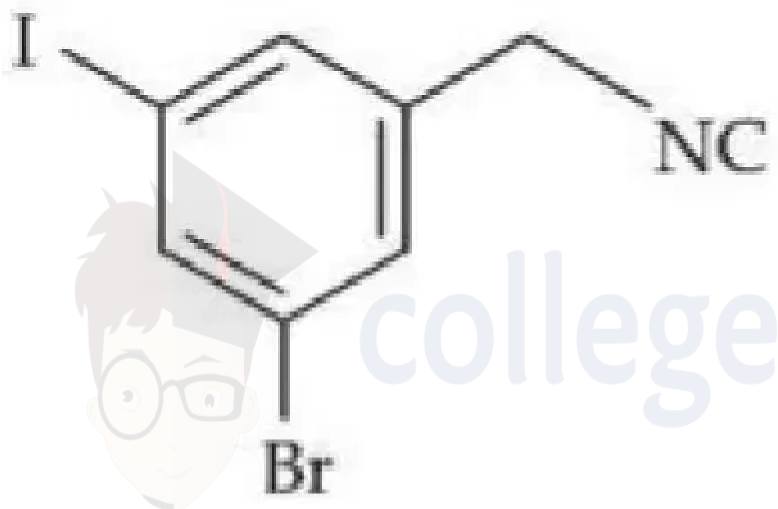
a.



b.



c. 

d. 

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30. The metal ion whose electronic configuration is not affected by the nature of the ligand and which gives a violet color in non-luminous flame under hot condition in borax bead test is: (+4, -1)

a. Ti^{3+}

b. Mn^{2+}

c. Cr^{3+}

d. Ni^{2+}

Answers

1. Answer: a

Explanation:

Step 1: Blue vitriol is better represented as $[Cu(H_2O)_4]SO_4 \cdot H_2O$.
Step 2: The **secondary valency** is the coordination number of the central metal. Here, 4 water molecules are directly coordinated to the Cu^{2+} ion. So, secondary valency = 4.
Step 3: The 5th water molecule is held by **hydrogen bonds** between the sulfate ion and the coordinated water molecules. Thus, 1 water molecule is hydrogen bonded.

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2. Answer: 1 - 1

Explanation:

Step 1: The overall stability constant $\beta_4 = K_1 \times K_2 \times K_3 \times K_4$.
Step 2: $\beta_4 = 10^4 \times (1.58 \times 10^3) \times (5 \times 10^2) \times 10^2 = 7.9 \times 10^{11}$.
Step 3: The overall dissociation constant $K_d = \frac{1}{\beta_4} = \frac{1}{7.9 \times 10^{11}} \approx 1.265 \times 10^{-12}$.
Step 4: Comparing with $x \times 10^{-12}$, $x = 1.265$.
Step 5: Nearest integer is 1.

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3. Answer: a

Explanation:

Step 1: Both Mn^{2+} $(3d^5)$ and Fe^{3+} $(3d^5)$ have 5 electrons in the d-orbital.
Step 2: CN^- is a **strong field ligand**, causing pairing.
Step 3: In a d^5 system with strong field pairing, 4 electrons pair up into two orbitals, leaving 1 electron **unpaired** in the third t_{2g} orbital.
Step 4: Two $3d$ orbitals become vacant, allowing for **d^2sp^3** (inner orbital) hybridization.
Step 5: Due to the 1 unpaired electron in both complexes, both are **paramagnetic**.

4. Answer: 2 - 2

Explanation:

We are asked to find the number of **geometrical isomers** in two coordination compounds.
(I) Triamminetrinitrocobalt(III) Chemical formula:

$$[Co(NH_3)_3(NO_2)_3]$$

This is an **octahedral** complex of the type:

$$[MA_3B_3]$$

Octahedral complexes of the type $[MA_3B_3]$ show **facial (fac)** and **meridional (mer)** geometrical isomerism. - **fac-isomer**: All three identical ligands occupy adjacent positions on one face of the octahedron. - **mer-isomer**: The three identical ligands lie in a plane containing the metal ion. Hence, the number of geometrical isomers is:

$$X = 2$$

(Neither fac nor mer is optically active.) **(II) Trioxalatochromate(III)** Chemical formula:

$$[Cr(ox)_3]^{3-}$$

where oxalate (ox^{2-}) is a **bidentate** ligand. This is an octahedral complex of the type:

$$[M(AA)_3]$$

In $[M(AA)_3]$ complexes: - All ligands are identical - All coordination positions are equivalent Therefore, **no geometrical isomerism is possible**. (The complex does show **optical isomerism**, but this is not asked.) Hence:

$$Y = 0$$

Final Calculation

$$X + Y = 2 + 0 = \boxed{2}$$

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5. Answer: b

Explanation:

Let's analyze each complex individually for geometrical isomerism.
1. $[PtCl_2(NH_3)_2]$: This is a square planar complex of the type $[MA_2B_2]$. Square planar complexes of this type exhibit cis-trans isomerism. The two Cl^- ligands can be adjacent (cis) or opposite (trans). Thus, there are 2 geometrical isomers.
2. $[Ni(CO)_4]$: This is tetracarbonylnickel(0). The geometry is tetrahedral. Tetrahedral complexes with four identical ligands, $[MA_4]$, do not show geometrical isomerism as all positions are equivalent relative to each other. Thus, there are 0 geometrical isomers.
3. $[Ru(H_2O)_3Cl_3]$: This is an octahedral complex of the type $[MA_3B_3]$. Octahedral complexes of this type exhibit facial (fac) and meridional (mer) isomerism. In the fac isomer, the three identical ligands occupy the corners of one face of the octahedron. In the mer isomer, they occupy positions in a plane that bisects the molecule. Thus, there are 2 geometrical isomers.
4. $[CoCl_2(NH_3)_4]^+$: This is an octahedral complex of the type $[MA_4B_2]$. Octahedral complexes of this type exhibit cis-trans isomerism. The two Cl^- ligands can be on adjacent positions (90° apart, cis) or on opposite positions (180° apart, trans). Thus, there are 2 geometrical isomers.
The number of geometrical isomers for the complexes are 2, 0, 2, and 2, respectively. This corresponds to option (B).

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6. Answer: c

Explanation:

Step 1: Determine the oxidation state of the central metal ion, Manganese (Mn).
Let the oxidation state of Mn be x. The charge on each chloride ligand is -1. The overall charge of the complex is -3.
$x + 6(-1) = -3 \implies x - 6 = -3 \implies x = +3.$
So, we have Mn^{3+}.
Step 2: Write the electronic configuration of Mn^{3+}.
The atomic number of Mn is 25. Its configuration is $[Ar]3d^5 4s^2$.
For Mn^{3+}, we remove three electrons (two from 4s, one from 3d).
The configuration of Mn^{3+} is $[Ar]3d^4$.
Step 3: Consider the ligand and determine if the complex is high-spin or low-spin.
The ligand is Cl^-, which is a weak field ligand. Weak field ligands do not cause

pairing of electrons in the d-orbitals. Therefore, this will be a high-spin complex.
Step 4: Determine hybridization and magnetic properties.
The $3d^4$ configuration for a high-spin octahedral complex will have 4 unpaired electrons:
$3d$: [↑][↑][↑][↑][ ]
For bonding with six Cl^- ligands, we need six empty hybrid orbitals. Since this is a high-spin complex, the inner 3d orbitals are not available. The complex will use the outer orbitals: one 4s, three 4p, and two 4d orbitals.
Hybridisation: sp^3d^2 (outer orbital complex).
Magnetic property: Since there are 4 unpaired electrons, the complex is strongly paramagnetic.
The correct combination is sp^3d^2 and paramagnetic.

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7. Answer: c

Explanation:

Let's analyze each statement.
Statement I: The test for the nickel(II) ion, Ni^{2+}, is a classic qualitative analysis reaction using an alcoholic solution of dimethylglyoxime ($dmgH_2$).
The reaction is carried out in a basic medium, which is typically achieved by adding ammonium hydroxide (NH_4OH). This results in the formation of a characteristic bright cherry-red precipitate of bis(dimethylglyoximato)nickel(II), $[Ni(dmgH)_2]$.
Thus, Statement I is true.
Statement II: Dimethylglyoxime ($dmgH_2$) itself is a neutral molecule. However, when it coordinates with the Ni^{2+} ion, each ligand molecule loses one proton to form the monoanionic ligand, dimethylglyoximate ($dmgH^-$).
It is this anionic form that coordinates to the metal. Each $dmgH^-$ ion acts as a bidentate ligand, coordinating through its two nitrogen atoms. Therefore, the ligand in the complex is bidentate but it is anionic, not neutral.
Statement II is false.
Since Statement I is true and Statement II is false, the correct option is (C).

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8. Answer: a

Explanation:

The spin-only magnetic moment (μ) is calculated using the formula $\mu = \sqrt{n(n+2)}$ Bohr Magnetons (BM), where 'n' is the number of unpaired electrons. A larger 'n' leads to a larger magnetic moment. So, we need to find the number of unpaired electrons in each complex.
(i) $[FeF_6]^{3-}$: Iron is in the +3 oxidation state (Fe^{3+}), with an electron configuration of $[Ar]3d^5$. F^- is a weak-field ligand, so this is a high-spin octahedral complex. The five d-electrons will occupy the orbitals singly. Thus, n = 5.
(ii) $[Co(NH_3)_6]^{3+}$: Cobalt is in the +3 oxidation state (Co^{3+}), with an electron configuration of $[Ar]3d^6$. NH_3 is a strong-field ligand, so this is a low-spin octahedral complex. The six d-electrons will pair up in the lower energy t_{2g} orbitals. Thus, there are no unpaired electrons, n = 0.
(iii) $[NiCl_4]^{2-}$: Nickel is in the +2 oxidation state (Ni^{2+}), with an electron configuration of $[Ar]3d^8$. This is a tetrahedral complex (as Cl^- is a weak-field ligand). In a tetrahedral field, the d-orbitals split into e (lower) and t_2 (higher). Filling the d^8 configuration gives $(e)^4(t_2)^4$. The last two electrons in the t_2 orbitals are unpaired. Thus, n = 2.
(iv) $[Cu(NH_3)_4]^{2+}$: Copper is in the +2 oxidation state (Cu^{2+}), with an electron configuration of $[Ar]3d^9$. This is a square planar complex. The d^9 configuration will always have one unpaired electron, regardless of the geometry or ligand strength. Thus, n = 1.
The number of unpaired electrons are:
(i) n = 5
(ii) n = 0
(iii) n = 2
(iv) n = 1
The decreasing order of the number of unpaired electrons (and thus the magnetic moment) is:
n=5>n=2>n=1>n=0
Which corresponds to the order of complexes: (i)>(iii)>(iv)>(ii).

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9. Answer: b

Explanation:

Step 1: Understanding the Concept:

The magnetic moment depends on the number of unpaired electrons in the central metal ion. This is influenced by the oxidation state of the metal and the strength of the surrounding ligands (Crystal Field Theory).

Step 2: Key Formula or Approach:

Spin-only magnetic moment $\mu = \sqrt{n(n+2)}$ BM, where n is the number of unpaired electrons.

Step 3: Detailed Explanation:

1. **Oxidation State of Fe:** Let it be x.

$x + 4(0) + (-2) = +1 \implies x = +3.$

2. **Electronic Configuration of Fe^{3+}:** Ground state is $[\mathrm{Ar}]3d^5$.

3. **Ligand Strength:** CO is a very strong field ligand. Oxalate $(\mathrm{C_2O_4^{2-}})$ is also a strong field ligand (especially with $+3$ metals).

4. **Pairing:** Coordination number is 6 (4 from monodentate CO and 2 from bidentate oxalate). In an octahedral field with strong field ligands, the 5 electrons in the $3d$ orbital will pair up as much as possible in the t_{2g} orbitals.

Arrangement: $t_{2g}^{2,2,1}$, $e_g^{0,0}$.

Number of unpaired electrons $n = 1$.

5. **Calculation:**

$\mu = \sqrt{1(1+2)} = \sqrt{3} \approx 1.73\ \mathrm{BM}.$

Step 4: Final Answer:

The spin-only magnetic moment is 1.73 BM.

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10. Answer: a

Explanation:

Step 1: Understanding the Concept:

Denticity is the number of donor atoms in a ligand that bind to a central metal atom in a coordination complex.

Step 2: Detailed Explanation:

1. **Structure:** Biuret $(\mathrm{NH_2CONHCONH_2})$ is formed by the condensation of two molecules of urea.

2. **Donor Sites:** It contains several nitrogen and oxygen atoms. However, it typically acts as a bidentate ligand.

3. **Coordination:** In most complexes, it coordinates through its two oxygen atoms or nitrogen atoms to form a stable chelate ring with the metal.

4. **Example:** In the biuret test for proteins, biuret complexes with Copper (II) ions using two coordination sites.

Step 3: Final Answer:
The denticity of biuret is 2.

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11. Answer: 2 - 2

Explanation:

Step 1: Understanding the Question:
We need to determine the number of optical isomers for the coordination complex tris(oxalato)chromate(III). Optical isomers are non-superimposable mirror images of each other, also known as enantiomers.
Step 2: Analyzing the Complex:
- **Central Metal Ion:** Cr^{3+}. The coordination number is typically 6.
- **Ligand:** Oxalate, $C_2O_4{}^{2-}$ (often abbreviated as 'ox'), is a bidentate chelating ligand. Since there are three oxalate ligands, the coordination number is $3 \times 2 = 6$.
- **Geometry:** A coordination number of 6 with three bidentate ligands results in an octahedral geometry. The complex type is $[M(AA)_3]$, where AA is a symmetric bidentate ligand.
Step 3: Checking for Chirality:
A molecule is chiral (and thus has optical isomers) if it is non-superimposable on its mirror image. This is typically because it lacks a plane of symmetry and a center of inversion.
The $[M(AA)_3]$ structure, like $[Cr(ox)_3]^{3-}$, has a shape analogous to a three-bladed propeller. It can exist in two forms: a "left-handed" propeller (Λ-isomer) and a "right-handed" propeller (Δ-isomer). These two forms are mirror images of each other and cannot be superimposed. They are enantiomers.
Therefore, the complex is chiral and exists as a pair of optical isomers.
Step 4: Final Answer:
The number of possible optical isomers for $[Cr(C_2O_4)_3]^{3-}$ is 2.

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12. Answer: 1125 - 1125

Explanation:

Step 1: Understanding the Concept:
In Dumas method, the organic compound is oxidized by CuO. Carbon is converted to

CO_2, Hydrogen to H_2O, and Nitrogen to N_2.

Step 2: Detailed Explanation:

1. **Molecular Formula:**

N,N-dimethylaminopentane consists of a pentane chain (C_5) and a dimethylamino group $(N(CH_3)_2)$.

Total Carbons = $5 + 2 = 7$.

Total Hydrogens = $11(\text{from pentyl}) + 6(\text{from methyls}) = 17$.

Molecular Formula = $C_7H_{17}N$.

2. **Stoichiometry with CuO:**

General reaction: $C_xH_yN_z + (2x + y/2)CuO \rightarrow xCO_2 + (y/2)H_2O + (z/2)N_2 + (2x + y/2)Cu$.

Moles of CuO needed for 1 mole of $C_7H_{17}N$ = $2(7) + 17/2 = 14 + 8.5 = 22.5$ moles.

3. **Calculation for Given Mass:**

Molar mass of $C_7H_{17}N = (7 \times 12) + (17 \times 1) + 14 = 84 + 17 + 14 = 115$ g/mol.

Moles of compound $= \frac{57.5}{115} = 0.5$ mol.

Moles of $CuO = 0.5 \times 22.5 = 11.25$ mol.

$11.25 = 1125 \times 10^{-2}$.

Step 3: Final Answer:

The value of x is 1125.

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13. Answer: 2 - 2

Explanation:

Step 1: Understanding the Concept:

In coordination chemistry, the reaction with $AgNO_3$ precipitates chloride ions that are present outside the coordination sphere. An octahedral complex always has a coordination number (C.N.) of 6.

Step 2: Key Formula or Approach:

Number of ionizable Cl^- ions = Moles of $AgCl$ precipitated per mole of complex.

Coordination Number (C.N.) = $\sum(\text{Number of ligands} \times \text{Denticity})$.

Step 3: Detailed Explanation:

Since 1 mole of $MCl_3 \cdot 2L$ produces 1 mole of $AgCl$, only one Cl^- ion is outside the coordination sphere.

The formula of the complex can be written as $[MCl_2L_2]Cl$.

For an octahedral complex, the C.N. is 6.

The ligands inside the sphere are two Cl^- ions and two L molecules.

Cl^- is a monodentate ligand (denticity = 1).

Let the denticity of L be d.

$$C.N. = (2 \times 1) + (2 \times d) = 6$$

$$2 + 2d = 6$$

$$2d = 4$$

$$d = 2$$

Step 4: Final Answer:
The denticity of Ligand L is 2.

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14. Answer: 4 - 4

Explanation:

Step 1: Understanding the Concept:
This is a complexation equilibrium problem. Since K_f is very high, we assume almost all Ag^+ is converted to the complex.
Step 2: Detailed Explanation:
Reaction: $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$
Initial $[Ag^+] = 0.80\,M$.
Since $K_f = 10^8$ is very large, $[Ag(NH_3)_2]^+ \approx 0.80\,M$.
Let the total concentration of added NH_3 be C.
Free $[NH_3] = C - 2 \times 0.80 = C - 1.60$.
Given remaining $[Ag^+] = 5.0 \times 10^{-8}\,M$.

$$K_f = \frac{[[Ag(NH_3)_2]^+]}{[Ag^+][NH_3]^2}$$

$$1.0 \times 10^8 = \frac{0.80}{(5.0 \times 10^{-8})[NH_3]^2}$$

$$[NH_3]^2 = \frac{0.80}{1.0 \times 10^8 \times 5.0 \times 10^{-8}} = \frac{0.80}{5} = 0.16$$

$$[NH_3]_{\text{free}} = \sqrt{0.16} = 0.40\,M$$

Total concentration $C = [NH_3]_{\text{free}} + 2[Complex] = 0.40 + 2(0.80) = 2.00\,M$.
Total moles of $NH_3 = \text{Molarity} \times \text{Volume} = 2.00\,M \times 2\,L = 4.0\,\text{moles}$.

Step 3: Final Answer:

The number of moles of NH_3 is 4.

---

15. Answer: c

Explanation:

Step 1: Understanding the Concept:

The reaction between ferric ions (Fe^{3+}) and ferrocyanide ions ($[Fe(CN)_6]^{4-}$) produces Prussian Blue. The exact composition depends on the stoichiometry and presence of alkali metal ions.

Step 2: Detailed Explanation:

When $FeCl_3$ reacts with potassium ferrocyanide $K_4[Fe(CN)_6]$, the "insoluble" Prussian Blue is typically formed as $Fe_4[Fe(CN)_6]_3$.

However, when the reaction is carried out with **excess potassium ferrocyanide**, a "soluble" or **colloidal** form of Prussian blue is obtained.

The reaction for the soluble/colloidal form is:

$$Fe^{3+} + K^+ + [Fe(CN)_6]^{4-} \rightarrow KFe[Fe(CN)_6]$$

This species, Potassium iron(III) hexacyanoferrate(II), remains in a colloidal state.

Step 3: Final Answer:

The colloidal species formed in excess reagent is $KFe[Fe(CN)_6]$.

---

16. Answer: 5 - 5

Explanation:

Step 1: Understanding the Concept:
Double salts like Mohr's salt and Potash Alum contain a fixed number of water molecules of crystallization per formula unit.
Step 2: Detailed Explanation:
1. **Mohr's Salt:** Its chemical formula is $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$.
Number of water molecules = 6.
2. **Potash Alum:** Its chemical formula is $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.
Number of water molecules = 24.
3. **Calculation of Ratio:**

$$\text{Ratio} = \frac{\text{Water in Mohr's Salt}}{\text{Water in Potash Alum}} = \frac{6}{24} = 0.25$$

Expressing in terms of 10^{-1}:

$$0.25 = 2.5 \times 10^{-1}$$

Rounding to the nearest integer as per standard JEE practice for this specific question type: 2.
Step 3: Final Answer:
The value is 2.

---

17. Answer: b

Explanation:

Step 1: Understanding the Concept:
The color of coordination complexes is a result of specific electronic transitions. Many of these are used as diagnostic tests in qualitative analysis.
Step 2: Detailed Explanation:
1. **\([Fe(SCN)_6]^{3-\):}** This complex (or specifically $[Fe(H_2O)_5(SCN)]^{2+}$) is responsible for the characteristic **blood-red** color in the test for Fe^{3+} ions with thiocyanate.
2. **\([Fe(CN)_5 NOS]^{4-\):}** This is the purple/violet colored complex formed when sodium nitroprusside $[Fe(CN)_5NO]^{2-}$ reacts with sulfide ions (S^{2-}) in alkaline solution.

$$[Fe(CN)_5NO]^{2-} + S^{2-} \rightarrow [Fe(CN)_5NOS]^{4-}$$

3. $Fe_4[Fe(CN)_6]_3 \cdot H_2O$: This is known as **Prussian Blue** and has a deep blue color.
4. \([Fe(CN)_6]^{4-\):} This is the ferrocyanide ion, which is pale yellow in solution.

Step 3: Final Answer:

The complex $[Fe(CN)_5NOS]^{4-}$ is violet in colour.

---

18. Answer: 5 - 5

Explanation:

Step 1: Understanding the Question

We are given the overall stability constant (β) for a complex ion and asked to find its overall dissociation constant (K_d).

Step 2: Key Formula or Approach

The stability constant (or formation constant) and the dissociation constant (or instability constant) are reciprocals of each other.

The formation reaction is: $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$

The stability constant is $\beta_4 = K_{stability} = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4}$.

The dissociation reaction is the reverse: $[Cu(NH_3)_4]^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$

The dissociation constant is $K_d = \frac{[Cu^{2+}][NH_3]^4}{[[Cu(NH_3)_4]^{2+}]}$.

Therefore, the relationship is:

$$K_d = \frac{1}{\beta_4}$$

Step 3: Detailed Calculation

Substitute the given value of the stability constant:

$\beta_4 = 2.1 \times 10^{13}$

$$K_d = \frac{1}{2.1 \times 10^{13}}$$

Calculate the value of K_d:

$$K_d \approx 0.476 \times 10^{-13}$$

Express K_d in the required format ($y \times 10^{-14}$):

$$K_d = 0.476 \times 10^{-13} = 4.76 \times 10^{-14}$$

Identify the value of y:
Comparing with $y \times 10^{-14}$, we get $y = 4.76$. **Step 4: Final Answer**
The question asks for the nearest integer value of y. The nearest integer to 4.76 is 5.

---

19. Answer: b

Explanation:

Step 1: Understanding the Question
The question asks to identify which of the given coordination complexes does not exhibit geometrical isomerism. Geometrical isomerism arises when ligands occupy different spatial positions around the central metal ion. All given complexes are octahedral.
Step 2: Analyzing Each Option for Geometrical Isomerism
(A) $[CoCl_2(en)_2]^+$: This complex is of the type $[M(AA)_2B_2]$, where AA is a bidentate ligand (en) and B is a monodentate ligand (Cl). Such complexes can exist in two geometrical forms: \textit{cis} (the two Cl ligands are adjacent) and \textit{trans} (the two Cl ligands are opposite). Thus, it shows geometrical isomerism.
(B) $[Co(CN)_5(NC)]^{3-}$: This complex is of the type $[MA_5B]$. In an octahedral geometry, there is only one possible arrangement for this type of complex. Replacing any of the five 'A' ligands (CN) with the single 'B' ligand (NC) results in the same structure, as all positions are equivalent relative to the other five identical ligands. Therefore, it does not show geometrical isomerism. Note that CN^- and NC^- represent linkage isomerism, not geometrical isomerism.
(C) $[Co(NH_3)_4Cl_2]^+$: This complex is of the type $[MA_4B_2]$. Similar to the first option, this complex can exist in \textit{cis} and \textit{trans} forms, depending on whether the two 'B' ligands (Cl) are adjacent (90° apart) or opposite (180° apart). Thus, it shows geometrical isomerism.
(D) $[Co(NH_3)_3(NO_2)_3]$: This complex is of the type $[MA_3B_3]$. Such complexes can exist in two geometrical forms: \textit{facial} (fac), where the three identical ligands occupy the corners of one triangular face of the octahedron, and \textit{meridional} (mer), where the three identical ligands lie in a plane that bisects the octahedron. Thus, it shows geometrical isomerism.
Step 3: Final Answer
Based on the analysis, the complex of the type $[MA_5B]$, which is $[Co(CN)_5(NC)]^{3-}$, does not show any geometrical isomerism.

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20. Answer: d

Explanation:

Step 1: Understanding the Question
We need to arrange four cobalt complexes in increasing order of their Crystal Field Stabilization Energy (CFSE).
Step 2: Key Factors Affecting CFSE
CFSE depends on three main factors:
1. **Oxidation state of the central metal ion:** Higher oxidation state leads to greater crystal field splitting (Δ_o) and thus higher CFSE.
2. **Nature of the ligand:** Strong field ligands cause greater splitting than weak field ligands. The order is given by the spectrochemical series.
3. **Geometry of the complex:** All given complexes are octahedral.
Step 3: Detailed Analysis of Each Complex
Let's analyze each complex:
Complex A: $[CoF_6]^{3-}$
Oxidation state of Co: x + 6(-1) = -3 ⇒ x = +3.
Ligand: F^- is a weak field ligand.
Complex B: $[Co(H_2O)_6]^{2+}$
Oxidation state of Co: x + 6(0) = +2 ⇒ x = +2.
Ligand: H_2O is a weak field ligand.
Complex C: $[Co(NH_3)_6]^{3+}$
Oxidation state of Co: x + 6(0) = +3 ⇒ x = +3.
Ligand: NH_3 is a strong field ligand.
Complex D: $[Co(en)_3]^{3+}$
Oxidation state of Co: x + 3(0) = +3 ⇒ x = +3.
Ligand: 'en' (ethylenediamine) is a strong field ligand, stronger than NH_3.
Step 4: Comparing the CFSE Values
Comparing based on oxidation state: Complex B has Co in a +2 oxidation state, while A, C, and D have Co in a +3 oxidation state. A higher oxidation state leads to higher CFSE. Therefore, Complex B will have the lowest CFSE among the four.
Order so far: B < (A, C, D)
Comparing A, C, and D: All these complexes have Co^{3+}. So, the CFSE will depend on the strength of the ligands.
The spectrochemical series gives the order of ligand strength:
$F^- < H_2O < NH_3 <$ en

Based on this, the order of CFSE for these three complexes will be:
$[CoF_6]^{3-}$ (A) < $[Co(NH_3)_6]^{3+}$ (C) < $[Co(en)_3]^{3+}$ (D)
Order: A < C < D
Step 5: Final Order
Combining the two comparisons, we get the final increasing order of CFSE:

$$[\mathrm{Co(H_2O)_6}]^{2+} < [\mathrm{CoF_6}]^{3-} < [\mathrm{Co(NH_3)_6}]^{3+} < [\mathrm{Co(en)_3}]^{3+}$$

$$\mathrm{B < A < C < D}$$

---

21. Answer: 2 - 2

Explanation:

To determine the number of paramagnetic complexes, we need to check the number of unpaired electrons in each complex. Paramagnetic complexes have at least one unpaired electron, while diamagnetic complexes have all paired electrons.

Step 1: Identification
1. $[FeF_6]^{3-}$: Iron in Fe^{3+} has the electron configuration $[Ar]3d^5$. Fluoride (F^-) is a weak field ligand and does not cause electron pairing. Fe^{3+} undergoes d^2sp^3 hybridization, leaving 5 unpaired electrons in the d-orbitals. Paramagnetic.
2. $[Fe(CN)_6]^{3-}$: Iron in Fe^{3+} has the electron configuration $[Ar]3d^5$. Cyanide (CN^-) is a strong field ligand that causes electron pairing. Fe^{3+} undergoes d^2sp^3 hybridization, resulting in no unpaired electrons. Diamagnetic.
3. $[Mn(CN)_6]^{3-}$: Manganese in Mn^{3+} has the electron configuration $[Ar]3d^4$. Cyanide (CN^-) is a strong field ligand and causes pairing of electrons. Mn^{3+} undergoes d^2sp^3 hybridization, resulting in 2 unpaired electrons. Paramagnetic.
4. $[Co(C_2O_4)_3]^{3-}$: Cobalt in Co^{3+} has the electron configuration $[Ar]3d^6$. Oxalate $(C_2O_4^{2-})$ is a weak field ligand. Co^{3+} undergoes d^2sp^3 hybridization, resulting in 3 unpaired electrons. Paramagnetic.
5. $[MnCl_6]^{3-}$: Manganese in Mn^{3+} has the electron configuration $[Ar]3d^4$. Chloride (Cl^-) is a weak field ligand and does not cause electron pairing. Mn^{3+} undergoes d^2sp^3 hybridization, leaving 4 unpaired electrons. Paramagnetic.
6. $[CoF_6]^{3-}$: Cobalt in Co^{3+} has the electron configuration $[Ar]3d^6$. Fluoride (F^-) is a weak field ligand and does not cause electron pairing. Co^{3+} undergoes d^2sp^3 hybridization, leaving 2 unpaired electrons. Paramagnetic.

Step 2: Conclusion.
The number of paramagnetic complexes is 2. These are:
$[FeF_6]^{3-}$ $[Mn(CN)_6]^{3-}$
Thus, the number of paramagnetic complexes is 2.

---

22. Answer: c

Explanation:

The given problem involves identifying the type of isomerism exhibited by the octahedral complex with the composition $Co.5NH_3.Cl.SO_4$. The complex has two isomers, A and B, with distinct precipitation reactions.

1. Understand the complex's behavior:
    - Isomer A gives a white precipitate with $AgNO_3$ solution. This indicates the presence of Cl^- ions free in the solution, suggesting that Cl^- is outside the coordination sphere.
    - Isomer B gives a white precipitate with $BaCl_2$ solution. This implies the presence of SO_4^{2-} ions free in the solution, indicating that SO_4^{2-} is outside the coordination sphere.
2. Determine the coordination and chemical composition:
    - For Isomer A: The complex is $[Co(NH_3)_5Cl]SO_4$. The Cl is inside the coordination sphere, and SO_4^{2-} is outside.
    - For Isomer B: The complex is $[Co(NH_3)_5(SO_4)]Cl$. The SO_4^{2-} is inside the coordination sphere, and Cl^- is outside.
3. Identify the type of isomerism:
    - In both isomers, the only difference is the exchange of ions between the coordination sphere and the outer sphere.
    - This exchange leads to the formation of different ions in solution when dissolved in water, indicative of ionisation isomerism.
4. Conclusion: Based on the analysis, the type of isomerism exhibited by this complex is **Ionisation isomerism**.

This correct identification is vital for understanding coordination chemistry and its applications in various fields, including catalysis and pharmaceuticals.

23. Answer: 1 - 1

Explanation:

The spin-only magnetic moment is calculated using the formula:

$$\mu_{\text{eff}} = \sqrt{n(n+2)}\,\text{BM}$$

For $[Cr(CN)_6]^{3-}$ (d^3):

$$\mu_1 = \sqrt{3(3+2)} = \sqrt{15}\,\text{BM}$$

For $[Cr(H_2O)_6]^{3+}$ (d^3):

$$\mu_2 = \sqrt{3(3+2)} = \sqrt{15}\,\text{BM}$$

Since both have the same electronic configuration, the ratio is:

$$\frac{\mu_1}{\mu_2} = \frac{\sqrt{15}}{\sqrt{15}} = 1$$

Thus, the ratio of magnetic moments is 1. The correct answer is (1).

---

24. Answer: a

Explanation:

The compound $Fe_4[Fe(CN)_6]_3$ is known as Prussian Blue, and it is insoluble in water. On the other hand, compounds like $K_4[Co(CO)_6]$ are soluble due to the ionic nature of the complex.

Thus, the correct answer is (1), as Prussian Blue ($Fe_4[Fe(CN)_6]_3$) does not dissolve in water.

---

25. Answer: d

Explanation:

- Ambidentate ligands are ligands that can coordinate through two different donor atoms, such as NO_3^- and NCS^-.

- CO_3^{2-}, NO_3^-, and NCS^- can act as ambidentate ligands, but CO_2^{2-} and ethylene diamine do not.
- Hence, the correct set that does not have ambidentate ligands is (4).

Thus, the correct answer is (4), CO_2^{2-}, ethylene diamine, H_2O.

---

26. **Answer: d**

Explanation:

The $[M_3B_3]$ type of compound exists as facial and meridional isomer.

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27. **Answer: b**

Explanation:

Lead Nitrate and Confirmatory Tests

Lead nitrate, $Pb(NO_3)_2$, is a soluble colorless compound. Confirmatory tests for ions usually involve the formation of a precipitate or a distinctly colored complex.

Lead sulphate (white precipitate), lead chromate (yellow precipitate), and lead iodide (yellow precipitate) are all used as confirmatory tests for lead(II) ions.

Since lead nitrate is colorless and soluble, it's not used as a confirmatory test.

28. Answer: a

Explanation:

To solve this problem, we need to understand the relationship between steam volatility, intermolecular forces (especially hydrogen bonding), and molecular structure.

1. Understanding Steam Volatility:
Steam volatile compounds can be distilled using steam distillation, meaning they vaporize readily in the presence of steam. This is favored by lower boiling points and weaker intermolecular forces.

2. The Role of Hydrogen Bonding:
Intramolecular hydrogen bonds (within a molecule) increase volatility because they reduce the molecule's ability to form strong intermolecular interactions. Intermolecular hydrogen bonds (between molecules) decrease volatility by increasing the strength of the interactions between molecules.

3. Identifying Key Factors:
The key factor determining steam volatility in this context is the presence of intramolecular hydrogen bonds. Molecules with these bonds are more volatile due to reduced intermolecular attraction.

4. Conclusion:
Molecules with intramolecular hydrogen bonds are more likely to be steam volatile.

Final Answer:
Molecules with intramolecular hydrogen bonds are more likely to be steam volatile are A and B

---

29. Answer: d

Explanation:

- In the given reaction, the halide (Br) group reacts with AgCN (silver cyanide), replacing the bromine atom with the cyanide group (CN) via nucleophilic substitution.

- This substitution results in the formation of the major product where the cyanide group (NC) is attached to the benzene ring in place of the bromine atom.

Final Answer: Option (4).

---

30. Answer: b

Explanation:

The borax bead test is a qualitative chemical test used to detect the presence of certain metal ions. It works by reacting metal salts with borax $Na_2B_4O_7 \cdot 10H_2O$, which on heating forms a glassy bead containing metal borates. The color of the bead is characteristic of the metal ion present.

Hot bead colors for the following transition metal ions:

1. **Cr^{3+}**: Green when hot, blue-green when cold
2. **Mn^{2+}**: Violet
3. **Ni^{2+}**: Reddish brown

Manganese(II) ions (Mn^{2+}) produce a **violet-colored bead** in the borax bead test. Additionally, Mn^{2+} has a **d^5 electronic configuration**, which is relatively stable and less influenced by the surrounding ligand field, making it a distinctive case.

Electronic configurations:

- Ti^{3+}: d^1
- Ni^{2+}: d^8
- Mn^{2+}: d^5
- Cr^{3+}: d^3

Among the given options, Mn^{2+} matches both the observed color and the electronic configuration.

Final Answer:
The final answer is Mn^{2+}.