CHM 102A QUIZ 2

Total Marks: 20 Duration: 30 minutes

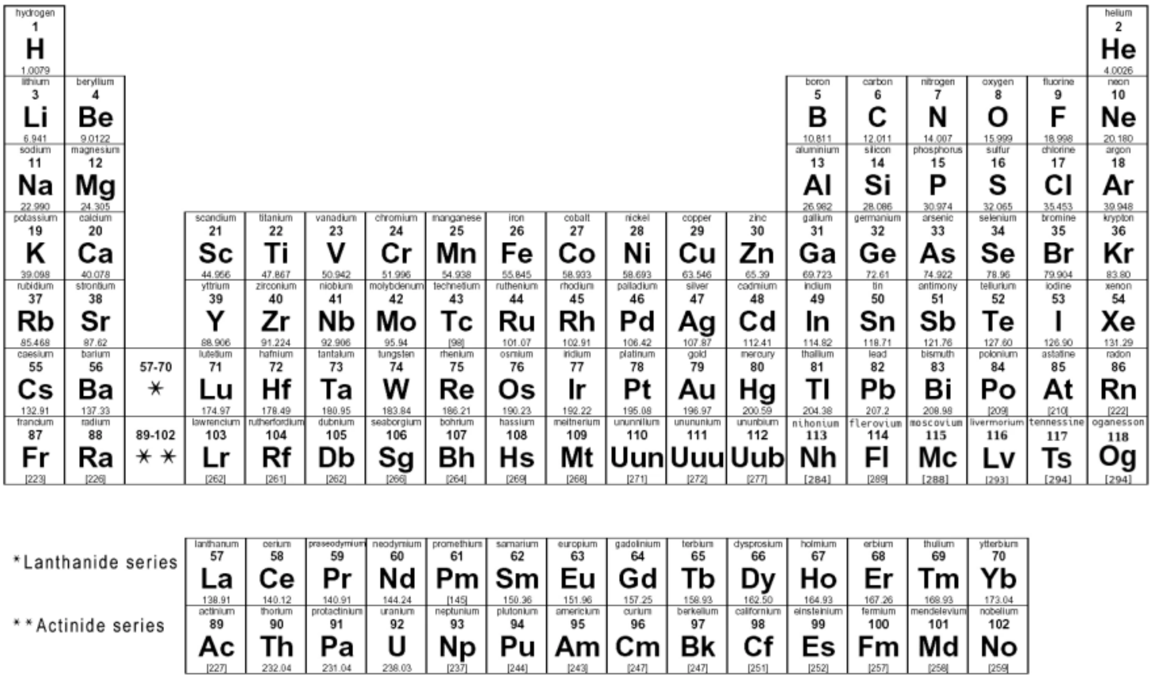
Name:

Roll Number:

Section:

Instructions:

1. ***Please write answers in the space provided (boxes).***
2. ***Please write in ink. (Answers written in pencil will not be re-graded)***



Q. No.	1	2	3	4	5	6	7	Total
Marks								

Q1. Co(III) forms octahedral complexes with the general empirical formula $CoCl_m \bullet nNH_3$.

a) What values of n and m are possible? **(1+1 = 2 marks)**

Answer:

m	**3**
n	**3, 4, 5, 6**

<u>1 mark each for m and n. All values of n must be correct to get 1 mark.</u>

Co(III) must have six ligands to form an octahedral complex. Also, it must have enough chloride ions to neutralize its 3+ charge. So, m must equal 3. With that known, it must have enough ammonia groups to achieve its octahedral structure, regardless of how many chloride ions are present. So, n can equal 6, 5, or 4 or 3.

In other words, for the given information, the complex could be any of the following: $[CoCl_3(NH_3)_3]$; $[CoCl_2(NH_3)_4]Cl$; $[CoCl(NH_3)_5]Cl_2$; $[Co(NH_3)_6]Cl_3$

b) Upon the addition of excess $AgNO_3$, one of the complexes precipitates 1 mole of AgCl for every mole of Co. What are the values of n and m for this complex? **(1+1 = 2 marks)**

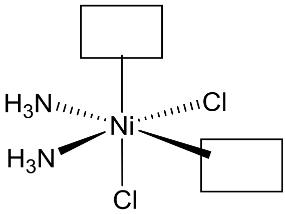
Answer:

m	**3**
n	**4**

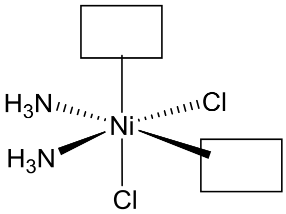
<u>1 mark each for correct value(s) of m and n.</u>

Only the free Cl- ions will precipitate with AgCl added. The other two Cl^- will be bound to the Co and will not precipitate. With this additional information, the identity of this complex would be $[CoCl_2(NH_3)_4]Cl$.

Q2. Fill in the missing ligands below to complete the structures of *fac*- and *mer*-$Co(NH_3)_3Cl_3$. **(1+1 = marks)**

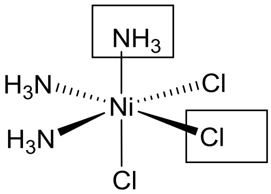


fac-$Co(NH_3)_3Cl_3$

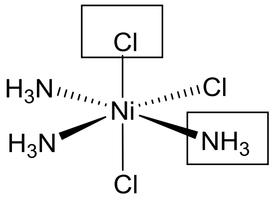


mer-$Co(NH_3)_3Cl_3$

Answer:



fac-$Co(NH_3)_3Cl_3$



mer-$Co(NH_3)_3Cl_3$

1 mark each for the right answer.

Q3. Assuming that the following complexes obey the 18 electron rule, answer the questions below:

a) Determine the identity of the 3d-transition metal M in $[(\eta^3\text{–}C_3H_5)M(CN)_4]^{2-}$. **(1 mark)**

Answer:

M =	**Co**

1 mark for the correct metal.

The complex has overall charge of -2 and it has one negatively charged ligand (η^3–C_3H_5). Therefore, the metal is in the +3 oxidation state.

The allyl anion contributes 4 electrons while the 4 cyanides donate a total of 8 electrons. Since the complex is electron precise, the number of electrons donated by M = 18 – (12) = 6.

Hence, M is a transition metal which has 6 electrons in its +3 oxidation state. So the answer is M = Co.

b) Deduce the number of metal-metal bonds that exist in $[(\eta^5\text{–Cp})Co(CO)]_2(\mu\text{-}CO)$. **(1 mark)**

Answer:

No. of M-M bond(s) =	**1**

<u>1 mark for the correct number of Co-Co bond.</u>

Counting the electrons for each Co:

Co(I)	8 electrons
Cp^-	6 electrons
CO	2 electrons
μ-CO	1 electron
TOTAL	17 electrons

To fulfil the 18 electron rule, each Co needs one electron which can be obtained by 1 Co-Co bond.

Q4.

a) Among the four metal ions given below, identify the two which form perfect octahedral complexes. (both metal ions have to be correct to get marks. No partial marking) **(1 mark)**

Ti(III), Cr (III), Ni(II), Cu(II)

Answer:

I	**Cr (III)**
II	**Ni (II)**

<u>1 mark for correct answers. Both answers have to correct to get 1 mark. No partial marking.</u>

Octahedral complexes of Cr(III) will have $t_{2g}^3e_g^0$ configuration which will not shot JT distortion. Ni(II) in octahedral complexes has the configuration $t_{2g}^6e_g^2$ which will also not show JT distortion.

b) Among the four metal ions given in part (a) above, identify which one shows the most prominent Jahn-Teller distortion. **(1 mark)**

Answer:

Metal ion with most prominent J-T distortion =	**Cu (II)**

1 mark for the correct answer.

Cu(II) has degeneracy in the e_g level so it will show most prominent JT distortion. Ti(III) has degeneracy in the t_{2g} level so distortion will be less prominent.

Q5. For each of the following pair of complexes, identify the one that has the larger crystal field stabilization energy (CFSE). **(1+1 = 2 marks)**

a) $[Cr(OH_2)_6]^{2+}$ or $[Mn(OH_2)_6]^{2+}$

Answer:

Complex with higher CFSE =	$\mathbf{[Cr(OH_2)_6]^{2+}}$

1 mark for right answer.

Both are high-spin complexes. While Mn^{2+} is a d^5 ion and hence CFSE = 0, Cr^{2+} is a d^4 ion and hence $[Cr(OH_2)_6]^{2+}$ has $t_{2g}^3\ e_g^1$ configuration and CFSE = $[(-0.4 \times 3) + (0.6 \times 1)]\Delta o = -0.6\ \Delta_o$. Thus, $[Cr(OH_2)_6]^{2+}$ has the larger CFSE.

b) $[Ru(CN)_6]^{3-}$ or $[Fe(CN)_6]^{3-}$

Answer:

Complex with higher CFSE =	$\mathbf{[Ru(CN)_6]^{3-}}$

1 mark for right answer.

Both Ru^{3+} and Fe^{3+} are d^6 ions that belong to the same group. Both complexes are low spin and hence have t_{2g}^6 electron configuration. However, Δ_o increases down the group and hence the ruthenium complex will have the higher CFSE.

Q6. Consider the complexes $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$ and answer the questions below: **(1 + 1 + 1 +1 = 4 marks)**

a) What are the geometries of these complexes?

Answer :

Complex	Geometry
$[Co(H_2O)_6]^{2+}$	**Octahedral**
$[CoCl_4]^{2-}$	**Tetrahedral**

b) What are the oxidation states of Co in these complexes?

Answer :

Complex	Oxidation State of Metal
$[Co(H_2O)_6]^{2+}$	**+2**
$[CoCl_4]^{2-}$	**+2**

c) Which of these complexes will have a higher magnetic moment?

Answer :

Complex with higher magnetic moment =	$[Co(H_2O)_6]^{2+}$

Both complexes have same number of unpaired electrons but orbital contribution is possible in $[Co(H_2O)_6]^{2+}$ which has electronic configuration $t_{2g}^5\ e_g^2$ whereas in $[CoCl_4]^{2-}$, the electronic configuration is $e^4\ t_2^3$ which cannot have orbital contribution.

d) Which of these complexes will show more intense colour?

Answer :

Complex which shows more intense color =	$[CoCl_4]^{2-}$

Q7. $[Ni(CN)_4]^{2-}$ is diamagnetic while the observed magnetic moment for $[NiCl_4]^{2-}$ complex is **2.8 B.M**. Assuming there is no significant orbital contribution, answer the following questions.

a) What are the geometries of the two complexes? **(1 + 1 = 2 marks)**

Answer:

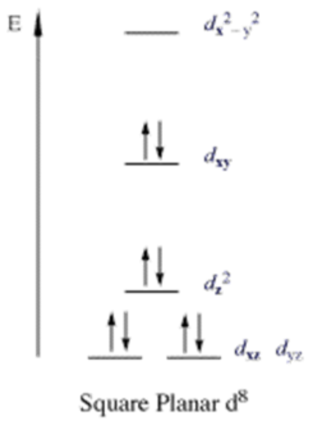
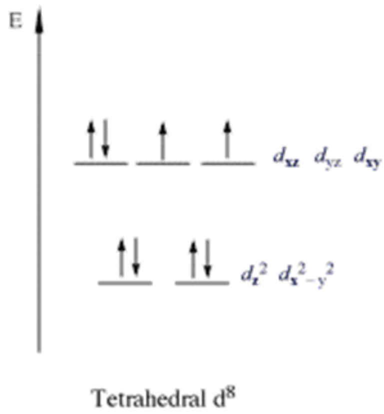
Complex	Geometry
$[Ni(CN)_4]^{2-}$	**Square planar**
$[NiCl_4]^{2-}$	**Tetrahedral**

b) Using principles of Crystal Field Theory, draw the *d*-orbital splitting diagram and show the electron distribution for both complexes. (Answer has to be completely correct to get 1 mark each. No partial marking.)

(1 + 1 = 2 marks)

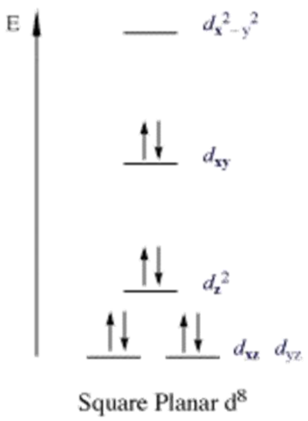
Answer:

Orbital splitting diagram and *d*-electron distribution for $[Ni(CN)_4]^{2-}$	Orbital splitting diagram and *d*-electron distribution for $[NiCl_4]^{2-}$

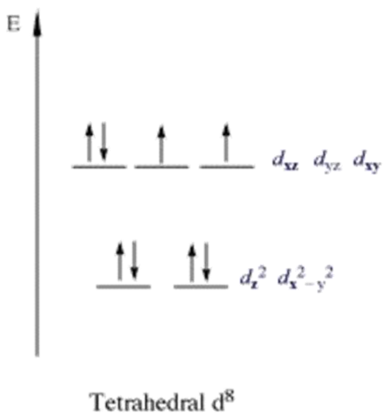
 $[Ni(CN)_4]^{2-}$	 $[Ni(Cl)_4]^{2-}$

Answer:

For $[NiCl_4]^{2-}$, $\mu = [n(n+2)]^{1/2}$ so n = 2. For a 4-coordinate complex, possible structures are tetrahedral or square planar and this is a Ni^{2+} d^8 ion. For a d^8 ion, a square planar geometry would result in no unpaired electrons (diamagnetic) and hence $[Ni(CN)_4]^{2-}$ is square planar. For d8 ion, a tetrahedral geometry would result in 2 unpaired electrons and hence $[Ni(Cl)_4]^{2-}$ turns out to be tetrahedral.



$[Ni(CN)_4]^{2-}$



$[Ni(Cl)_4]^{2-}$

1 mark for each correct answer.